CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

A PRACTICAL TEXT-BOOK.

BY

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F.I.C., ASSOC.INST.C.E.,
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TO THE CROWN AGENTS
FOR THE COLONIES.

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PREFACE TO SECOND EDITION.

THE first volume of this book was written on somewhat unusual lines, and failed on this account to obtain conventional regard. The Authors, far from being penitent, consider that their effort was successful, and after a proper lapse of time, and with the aid of effective lieutenants, put forward the present edition, which, whilst preserving the essence of the earlier, is intended to give better and (of course) later information.

Their thanks are particularly due to Mr. Gilbert J. Alderton, B.Sc.(Lond.), F.I.C., in whose hands the revision of the first volume has remained when that work was relinquished by Mr. Arthur G. Levy, B.Sc. (Lond.), F.I.C., on his leaving this country.

B. B.
A. G. B.

July, 1911.

PREFACE TO FIRST EDITION.

In writing the present book the authors have had chiefly in view the needs of Practising Engineers, Managers of Works, and Technical Students desirous of obtaining some knowledge of Chemical Technology.

In a book of this scope, lengthy descriptions of plant and of processes which differ from each other merely in detail would be out of place. For this reason, only such processes are described as are typical of the class to which they belong.

The adoption of this plan has given opportunity for presenting the subjects dealt with in a manner which shows their relations to each other. It is hoped, therefore, that the book as a whole may prove useful even to the expert in any one of the subjects touched upon. In order to achieve this degree of usefulness the authors have specially endeavoured to explain the general principles underlying each process, even when the working details appear complex and arbitrary.

Vol. I. includes the chemical principles of subjects which are of particular interest to the Mechanical Engineer, to

the *Architect* and *Builder*, and to all Manufacturers who are concerned in the erection of plant and the production of power. The information given is designed to be of so practical a character as will enable an owner of machinery or user of power to detect causes of bad economy, and to realise when saving may be effected by calling in expert assistance.

Vol. II. treats of the chief manufactures which have a chemical basis. The authors trust that for many readers, especially students of manufacturing chemistry, the information given will be found adequate to afford a sound groundwork of knowledge without proving as difficult to grasp as is the mass of facts proper to a monograph.

LONDON, *December*, 1897.

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CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

VOL. I.

CHEMISTRY OF ENGINEERING, BUILDING, AND METALLURGY.

CHAPTER I.

THE CHEMISTRY OF THE CHIEF MATERIALS OF CONSTRUCTION.

THE permanency of a given structure and the degree in which it is fitted for its use, do not depend exclusively upon the mechanical strength of the materials composing it, but are largely influenced by the chemical composition of these materials and by the chemical conditions to which they are exposed. It follows, therefore, that a knowledge of the chemistry of the chief materials of construction is necessary in deciding of what material a given structure is to be built.

STONE, BRICK, AND CONCRETE.

A rough classification of natural stones used at all largely for building purposes, may be made by dividing them into the groups *siliceous* and *calcareous*. The following are brief descriptions of the chief building stones commonly used :—

1. **SILICEOUS STONES.**—**Sandstone** is composed of grains of quartz (*silica*) cemented together to form a coherent mass.

Its value as a building material depends largely on the substance cementing the grains of quartz together, as on the removal of the agglutinant, disintegration of the stone naturally follows. The nature of the agglutinant varies considerably. Siliceous matter itself sometimes constitutes the cement and the stone is then a mass of nearly pure silica, and is both refractory to weathering and difficult to work. An argillaceous cementing material (composed essentially of silicate of alumina) is more easily attacked than a siliceous agglutinant, and the sandstones containing the former are, therefore, less refractory to weathering than those held together by the latter. A special form of sandstone, laminated by layers of micaceous matter, is that known as *Yorkshire flagstone* and used for street paving and making acid-proof apparatus—*e.g.*, chlorine stills (*q.v.*, Vol. II.). For the latter purpose the laminar character of the stone and its freedom from cementing material other than siliceous matter constitute the advantages which it presents. Felspar also occurs as a cementing material of sandstone. (When the felspar is more or less decomposed into kaolin the sandstone falls into the argillaceous category.) Much *millstone grit*, which is a coarse grained sandstone, very tough and resistant, is thus cemented. Other cementing materials of less importance are oxides of iron, giving the sandstone a yellow, brown, or blue colour, according to the state of oxidation of the iron. The presence of iron pyrites, which sometimes occurs in sandstone, tends to bring about the disintegration of the stone on weathering by the oxidation of the pyrites. Sandstones cemented with iron oxides are less permanent in character than those held together by siliceous agglutinants. Barium sulphate has also been found to exist as a cementing material of certain sandstones.

A cementing material comparable in importance with those of the siliceous class, is the calcareous matter frequently found fulfilling this function. Such sandstones are held together by calcium carbonate and are more readily worked than the siliceous variety, coming in this respect under the head of *free-stones*—*i.e.*, stones which can be easily sawn and wrought into shape without chipping and grinding. Such sandstones are, however, somewhat easily attacked by weathering, as will be explained at the end of this chapter. Besides the cementing material of a sandstone, the size and shape of the constituent grains are of importance in influencing the character of the stone. Thus, in sandstone of ideal quality from the point of view of mechanical strength and non-porosity, the grains should be of such assorted sizes as to leave a minimum amount of space either unoccupied or filled by the cementing material. The

statement that the coarser the grain the more durable the sandstone (other things being equal), is not based on satisfactory experimental evidence. With regard to resistance to weathering, especially to the action of frost, it has been recently shown that a less porous stone is not necessarily more resistant than one more porous, as the latter allows room for the expansion of the absorbed water in freezing and suffers less disintegration (*v.i.*). Obviously, this possession of spaces capable of affording room for expansion in freezing may compensate for the tendency of such a stone to absorb and hold a large quantity of water. The following analyses of sandstone grits are typical :—

	Grit, Cambrian (Barmouth).	Carboniferous Millstone Grit (Cumberland)
Moisture,	0·125	0·050
Combined H_2O,	0·935	1·290
SiO_2,	80·600	87·400
Al_2O_3,	9·200	3·997
CO_2	1·025	1·876
P_2O_5,	0·076	Trace.
SO_3,	Trace.	0·060
Fe_2O_3,	Trace.	...
FeO,	2·370	1·366
MnO,	0·232	0·279
FeS_2,	...	0·300
CaO,	1·330	1·932
MgO,	1·285	0·684
K_2O,	1·647	0·741
Na_2O,	1·372	0·332
	100·197	100·307
Specific gravity,	2·689	2·710

Granite consists of a mixture of *felspar* (usually a double silicate of alumina and potash or soda—*e.g.*, orthoclase, $6SiO_2 . Al_2O_3 . K_2O$—or of alumina, lime and soda—*e.g.*, oligoclase, $3SiO_2 . Al_2O_3 . CaO . Na_2O$) *quartz* (silica), and *mica* (a double silicate of alumina and magnesia, potash or soda—*e.g.*, $4MgO . Al_2O_3 . 4SiO_2$*). An average proportion of these constituents is 40 to 50 per cent. of felspar and 40 to 30 per cent. of quartz, the remainder being mica. A large proportion of mica, especially in plates of an appreciable size, causes the granite to polish

* The complexity of mica, owing to the replacement of one oxide by another, is such that its general formula may be written

$$4(K_2MgFe)O . (AlFe)_2O_3 . 4SiO_2.$$

badly and to fade quickly. The mica is only, as it were, a filling; the quartz and felspar are the constituents of granite which are of real mechanical importance. *Syenitic granites* have the mica partially or wholly replaced by *hornblende* ([FeMg]O . SiO_2) which is generally black in colour. It is evident that this range of composition involves a corresponding range of appearance and properties of granites. A granite containing much quartz and a stable form of felspar is refractory to destructive agencies, but hard and difficult to work. Such a stable form of felspar is generally vitreous and transparent, allowing the light to penetrate the rock and to be reflected from the darker constituents. A soft earthy felspar is opaque, and causes the granite to appear lighter in colour; hence it happens that conspicuously white granites are usually little resistant to weather. The colour of granite may vary from grey to red. The former colour is due to the magnesia mica (*biotite*), the latter to a red variety of potash felspar (*orthoclase*). Iron stains in the granite indicate unsoundness, and granite in which the felspar is earthy in appearance is also inferior (*v.s.*). Granite, being an igneous rock—that is, one which has solidified after fusion, probably under pressure—is impervious and non-porous, and suffers destruction exclusively from without. Its permanence depends on the size and degree of coherence of its constituent minerals, the close-grained kinds, formed of small interlocking crystals, being the most refractory to destructive agencies. Syenitic granites are harder and generally more durable than ordinary granites.

Gneiss, which is a granite in which the mica occurs stratified, is also used to a certain extent as a building material. *Whinstone* and *trap* (both known as "greenstone" from their colour) are also igneous rocks used for building, and consist chiefly of felspar and hornblende.

2. **CALCAREOUS STONES.—Marble** in the strict sense is calcium carbonate, approximately pure, crystallised as calcite. There is no hard and fast line between limestone and marble, but by general consent the latter term is applied to those forms of calcium carbonate which have a well-marked crystalline fracture, like that of loaf-sugar. It appears that marble has been formed geologically by the heating to a plastic condition of forms of calcium carbonate, of looser structure, under pressure sufficient to prevent the escape of CO_2, which would otherwise have been eliminated below the temperature of fusion. This change has been effected experimentally by Le Chatelier, who found it to occur at 1,020° C. = 1,868° F., an hour's exposure sufficing to produce artificial marble. The purest form of marble is white and without veins, *Carrara marble* serving as

an example.* The colours of marbles other than white are due to the presence of various impurities. Thus, ordinary white marble with dark veins is coloured with metallic oxides—*e.g.*, those of iron: red marbles are also coloured with iron as ferric oxide, and black marble owes its colour to bituminous matter, as much as 1·48 per cent. of carbon having been found in an Irish specimen. Some marbles are distinguished by markings due to enclosed fossils—*e.g.*, those from Derbyshire. In addition to the above varieties, certain siliceous stones are often commercially termed "marble," although in no sense true marble. Thus, **serpentine,** which is an hydrated magnesium silicate containing iron, is frequently called "marble," but is distinguished physically (apart from its chemical difference) by its structure, which is not crystalline. The following are analyses of serpentine:—

	Per cent.	Per cent.*
SiO_2,	33·80	40·06
Al_2O_3,	1·65	1·37
Cr_2O_3,	0·42	0·20
FeO,	9·79	3·43
ZnO,	0·30	...
CaO,	3·46	...
MgO,	31·74	30·02
Na_2O,	0·32	...
MnO,	Trace.	0·09
NiO,	Trace.	0·71
CO_2,	5·66	...
Combined water,	12·86	12·10
	100·00	..

Alabaster (hydrated calcium sulphate) is also termed "marble" in the trade. Marble is only used for ornamental building, except when its abundance at the spot where it is to be used makes it sufficiently cheap as a structural material. The waste of marble cutting is powdered and used for making CO_2 for preparing aerated waters.

Limestone is a compact form of calcium carbonate, ranging from a material somewhat less definitely crystalline than marble to one devoid of crystalline structure. The **carboniferous limestones** are very compact: **lias limestone** is also compact, but contains a good deal of clay (see *Cement*, Vol. II.). **Kentish rag**

* This analysis is incomplete, but shows the characteristic constituents of a serpentine.

is a tough limestone containing clayey material, and often coloured with oxide of iron. Some varieties will not bear weathering. The structure of many limestones resembles that of sandstone, being granular: an example is furnished by **oolitic limestone**, the granules of which are large, definite and rounded. **Portland stone** is an oolitic limestone. **Bath stone** is very variable in quality, some varieties withstanding weather well and others being easily disintegrated: it is easily worked, and hardens after exposure to air. The more nearly limestones approach marble in structure, the more durable they are. **Purbeck stone** is a shelly limestone consisting largely of small fossil shells. Besides these, which are approximately pure limestones, others are found intermixed with serpentine and similar siliceous minerals. True **dolomite** is a double carbonate of calcium and magnesium, corresponding with the formula $CaCO_3 . MgCO_3$: it ranges from this composition to that of ordinary limestone (which always contains a small proportion of magnesium carbonate); it is a hard and durable stone. The nearer a **magnesian** or **dolomitic** limestone approaches the composition of true dolomite, the more durable it is.

All the above calcareous stones are from their nature less fitted to withstand the action of weak acids than are the siliceous stones previously described. The causes of their destruction will be dealt with later.

Artificial stone is considered in the section on *Cements*, Vol. II., p. 154.

3. **BRICKS** * may be regarded as blocks of artificial sandstone with more cementing material than that which is present in the natural varieties. In the trade many kinds are known by name, but they cannot here be considered individually. **Kiln-bricks** are more uniformly burnt and more generally reliable than **clamp-bricks**,† which are apt to be unevenly burnt, many of them (particularly those on the outside of the clamp—"place bricks") being often soft from insufficient burning. On the other hand, those near the flue-holes of the clamp are usually over-burnt. (For the construction of kilns used in brick-burning, see section on *Clay Industries*, Vol. II.). Clamp-burnt bricks are classified according to the preparation of the clay of which they are made into **malms, washed** and **common stock.** The first-named are made from clay which has been ground with chalk, so as to make an artificial gault brick (*v.i.*): the second are made from clay freed from gross impurities by washing: and the last

* See also section on *Clay Industries*, Vol. II.

† The rectangular heap of bricks, itself constituting the walls and flues of the furnace, is known as a "clamp."

are manufactured from the untreated clay. Each clamp of each kind yields bricks differing in quality according to their burning, involving a further classification which is a matter of purely trade interest. The following among the less ordinary kinds require separate mention.

Red bricks are usually made from a fairly clean clay, nearly free from lime (which would produce a yellow tint), and containing a good deal—*e.g.*, 10 per cent.—of ferric oxide, to which their colour is due. The following is an example of such a clay in the air-dried state :—

	Per cent.
Insoluble silicates and sand,	39·26
Combined silica,	23·12
Alumina,	14·02
Ferric oxide,	8·39
Lime,	1·63
Magnesia,	3·45
Potash,	2·96
Soda,	0·15
Moisture,	1·68
Combined water, organic matter, and loss,	5·34
	100·00

Gault bricks are made from gault clay, which contains some 25 per cent. of calcium carbonate. They are light in colour and easily fusible, and thus need special care in burning.

Blue bricks are made from highly ferruginous clay, the iron in which is reduced to the state of magnetic oxide in the process of burning. They are fired at a clinkering temperature, and are therefore sintered together and less porous than ordinary bricks, while their mechanical strength is greater (*v.i.*). A common kind of blue brick is only superficially " blue," having received a coating of ferric oxide previously to being burnt. Such bricks are weaker and more pervious (as soon as the outer surface is destroyed) than genuine blue bricks, which are sintered throughout their mass. The standard size and weight of a common brick are 8¾ inches × 4¼ inches × 2½ inches, and 7 lbs. respectively. Special shapes and sizes—*e.g.*, for curved structures—are also made.

Fire bricks differ from ordinary bricks in that they are made of clay nearly free from oxides capable of acting as fluxes—*e.g.*, ferric oxide, lime, magnesia, and alkalies. There are two classes of ordinary siliceous fire bricks, viz. :—(1) Those composed of a true refractory clay (silicate of alumina), to which refractory sand or burnt refractory clay has been added to prevent undue shrinkage in drying and firing ; and (2) those composed of nearly

pure silica, with a minimum of foreign oxides capable of serving as cementing material. These types are illustrated by *Stourbridge* and *Dinas* fire bricks respectively; analyses of such clays are appended :—

	Plastic Fire Clay.	Dinas "Clay."
Quartz,	36·3	95·94
Combined silica,	27·0	1·68
Alumina,	23·3	1·40
Ferric oxide,	...	0·49
Ferrous oxide,	1·8	...
Lime,	0·7	0·29
Water and organic matter,	10·3	...
Alkalies,	...	0·20
	99·4	100·00

Bricks of these materials are burnt in kilns at a high temperature, in order that they may not alter in volume when in place in the furnace in which they are to be used. Dinas "clay" is found as a loose sand, and requires the addition of a small percentage of lime as a cementing material. **Ganister,** which is a similar material to Dinas clay, is found as a sandstone, and for furnace lining is generally ground and moulded *in situ.* Highly siliceous bricks usually expand when strongly heated, whereas those made from plastic clay contract.* The size and shape of fire bricks are even more various than those of ordinary bricks, on account of the need for accurate fitting of furnace linings.

The foregoing bricks are "acid" in character—*i.e.*, being composed largely of free silica (quartz), they are capable of acting as an acid material at high temperatures, and of fluxing in contact with a basic substance, such as lime. The more nearly a fire brick approaches kaolin in composition—*i.e.*, the smaller the proportion of free silica it contains—the less marked are its acid properties and the better is its resistance to basic fluxes. On increasing the proportion of alumina until an ultimate composition corresponding with that of bauxite is reached, a nearly "neutral" brick is obtained capable of withstanding fairly the action of both acid and basic oxides. A typical composition of a **bauxite brick** is Al_2O_3 70·7 per cent., Fe_2O_3 13·6 per cent., SiO_2 15·7 per cent.

Chromite (chrome iron ore) has also been used to furnish a

* Such bricks require an allowance of one-eighth of their linear dimensions for shrinkage in drying and burning.

fairly neutral brick, having an average composition of Cr_2O_3 50 per cent., FeO 30 per cent., Al_2O_3 15 per cent., SiO_2 5 per cent. Such a material is often used on account of its approximate neutrality, in order to separate acid and basic bricks (*v.i.*) when both are used to line one furnace, the former being generally adopted for arches where mechanical strength is necessary, and the latter for bottom linings where basic materials have to be fused, or (as in a steel furnace) where a basic condition is requisite.

Carbon bricks have been prepared from retort carbon, ground, mixed with tar, and burnt; they are not only neutral in character but have little tendency to alter in volume in the furnace, and are bad conductors of heat.

Soapstone (magnesium silicate, $6MgO \cdot 5SiO_2 \cdot 2H_2O$) has also been used as a neutral furnace lining; it is, however, attacked by basic materials.

Basic bricks, which are largely used in steel making by the basic process, are prepared either from dolomite (double carbonate of calcium and magnesium), or from magnesite (magnesium carbonate). The former substance, though burning to a hard and refractory state, slowly slakes and disintegrates on exposure to air: the latter is free from this defect. Both substances are more commonly used to line furnaces *in situ* by ramming the crushed material, mixed with tar, so as to form a layer on the surface of the bottom. Actual bricks are usually prepared from magnesia, moulded under heavy pressure and burnt at a high temperature. The best form of crude magnesia for basic bricks is that prepared by calcining Styrian magnesite, and has the composition—MgO 77·6 per cent., CaO 7·3 per cent., Al_2O_3 and Fe_2O_3 13·0 per cent., SiO_2 1·2 per cent. The impurities present aid the sintering of the brick to a compact mass. Magnesia, when "dead-burnt" at a high temperature, is devoid of plasticity, and in order to be moulded must be mixed with half its volume of lightly burnt magnesia, or a little magnesium acetate or chloride. Magnesia bricks do not flux with acid bricks below 1,600° C. = 2,912° F., but above that temperature slag readily; their behaviour with neutral alumina bricks is similar. They are used for lining basic steel furnaces, cement kilns, furnaces for reburning strontia in sugar works (see *Sugar*, Vol. II.), and for lead smelting works, being tight to that metal and to its oxide which readily penetrates acid bricks. Although all fire bricks (acid and basic) are commonly termed refractory, yet the term is over-wide unless the conditions under which the bricks are to be used are specified. Such bricks may be properly termed infusible—*i.e.*, at industrial temperatures. It is proper to observe that there is a difference between

infusibility and refractoriness. Both "acid" fire bricks, *i.e.*, those consisting mainly of silica, and "basic" bricks, *e.g.* those composed of lime and magnesia, are infusible at any temperature commonly employed, but they may only be called refractory when the conditions under which they are used are accurately defined. Thus acid bricks are unattacked by silica and acid silicates, but are corroded by mixtures containing a preponderance of basic oxides, the reverse being true of basic bricks (*cf.* the remarks on the subject under *Cement*, Vol. II.).

4. **CONCRETE** consists of a mixture of "cement mortar" with an "aggregate." By cement mortar is meant a mixture of sand and cement, as distinct from one of sand and lime constituting common mortar. The aggregate is simply some form of broken stone or pebbles that happens to be readily available at the place where the mortar is made. The advantage of concrete over all other building materials is that usually only one (and that the least weighty) of its constituents has to be brought from a distance—viz., the cement. The concrete is either made in blocks * near the place of use, and slung into position, or laid *in situ*—that is, placed when freshly mixed and still plastic in its ultimate position as part of the structure. An extreme form of such adaption is afforded by "grouting," in which a thin cement mortar is forced as a semi-fluid to fill spaces not otherwise accessible. With regard to the sand used in making cement mortar, it may be said that it should be sharp, fairly coarse, clean, and free from clay, loam, or peat. The aggregate must be chemically indifferent to the cement, and must have a fairly high compressive strength. It should preferably be in angular fragments of irregular size, and with a moderately rough surface, to favour the adherence of the cement. Clean "burnt ballast,"† fragments of hard limestone, granite chippings, broken brick, and the like are serviceable as aggregates. The proportion of sand to aggregate and of cement to both must be so adjusted that unfilled spaces between adjacent fragments of aggregate may be as few and small as possible, and the concrete block "solid" throughout. With aggregate and sand of ordinary quality a mixture of 1 part of cement, 2 of sand, and 4 of aggregate by volume makes a good concrete, though frequently mixtures much poorer in cement are used. In making concrete, thorough mixtures of the ingredients must be secured, and the water must be added by sprinkling, so as to get the mass uniformly wet. A porous aggregate may require previous wetting to ensure the presence of sufficient

* Huge blocks of concrete, which may be regarded as artificial monoliths, are much used in heavy harbour work.

† This material is burnt clay: "Thames ballast" is gravel.

water for the setting of the cement, and the surface to which the plastic mass is to be applied may also need wetting for the same reason. Regard must be had to the setting time of the cement (which varies largely with different specimens, *v.i.*), in order that the concrete may be got into place before setting has begun; otherwise, the half-set cement will be disturbed and its coherence impaired.

The objection to concrete for purposes where a space has to be spanned is that its tensile strength is comparatively low. During the past few years the practice of embedding iron and steel in the substance of the concrete for the purpose of strengthening it has grown rapidly in favour. Such "*re-inforced concrete*" (ferro-concrete) may, therefore, be described as Portland cement concrete with iron or steel embedded in such a manner that both materials, intimately connected with one another, can jointly exercise a statical effect against external forces. In this way advantage is taken of the high tensile strength of the iron or steel and the high compressive strength of the concrete. The statical co-operation of the two materials, otherwise so unequal, is based on the following accepted facts:—(*a*) The concrete, when well made, protects the enveloped iron against oxidation. (*b*) The adhesion of Portland cement to iron is very considerable, and nearly equal to the shearing strength of the concrete. (*c*) The coefficient of linear expansion through change of temperature of concrete and steel is nearly equal. Experience has shown that safe protection against rust and a sufficient adhesion can only be obtained if the proportion of cement in the mixture is not too meagre, and if the concrete is sufficiently impervious. The utility of re-inforcement has led to the development of many systems of construction, similar among themselves, and having proprietary titles. Their principle is sound, and they have proved successful in practice. The most successful methods are those in which the re-inforcement is in divided forms, these being arranged so that the stresses encountered may be adequately met. The application of this is to be found in the almost general use of rods, light bars, and expanded metal. The system is adapted for the erection of fire-proof buildings, light bridges of moderate span, and for the manufacture of pipes of large diameter.

The cement used in making concrete is necessarily not an **aerial cement** such as common mortar. By an **aerial cement** as distinct from an **hydraulic cement** is meant one that hardens by exposure to air, the hardening being due to desiccation and carbonation. In the heart of a concrete block both operations would occur so slowly as to prevent setting in a reasonable time.

Moreover, common aerial mortar is too weak mechanically to bear the large dilution with inert sand and aggregate, which is perfectly suitable for a strong hydraulic cement. In addition, much concrete is used under water, and its cement portion must be unattacked by water after the first hydration, which causes its setting. The cements used for concrete are, therefore, always strong hydraulic cements. **Portland cement** is most largely employed, though **Roman cement, puzzuolana cement, slag cement,*** and **hydraulic lime** are also thus utilised. (For a description of the manufacture and cause of setting of these cements, see the section on *Cement*, Vol. II.) Besides being used for making concrete, cement is employed for preparing cement mortar—*i.e.*, ordinary mortar with the lime replaced wholly or partly by cement. It is used in the same way as common mortar where extra strength or resistance to water is required. It is also used for facing work, lining tanks and reservoirs, etc., on account of its imperviousness. "Neat" (unmixed) cement is but little used, as when spread as a facing it is liable to crack from irregular contraction.

Ordinary **mortar** should be made from good "fat" lime (see *Lime*) and sharp sand (1 : 3 by vol.), free from loam and earthy matter. Cow hair is often incorporated to aid its coherence. Much benefit is claimed to be exerted upon the quality of lime mortar by the admixture of about 5 per cent. of plaster of Paris. This admixture is said to hasten the setting of the mortar and to increase its strength.

The chief necessities, other than the character of the aggregate, for the production of good concrete, are that the cement should be used in fair quantity (*e.g.*, 1 of cement to 6 of aggregate plus sand by vol.), and that it should be sound and strong. These qualities are ascertained in the following way :—

TESTING HYDRAULIC CEMENT.—The criteria which are generally determined are :—

1. **Fineness.**—The cement is sifted through standard sieves, and the percentage of residue remaining on these ascertained. A good finely-ground Portland cement should have a residue not exceeding 3 per cent. on a sieve having 76 meshes per linear inch, made of wire having a diameter of 0·005 inch. Much modern cement is even more finely ground than this. It is

* Amongst slag cements, the Passow cement deserves special mention. It is prepared by the regulated cooling of slag, two kinds of particles differing in chemical activity being obtained. These particles are then ground together, forming the cement. It is usual to add 10 per cent. of Portland cement to the mixture, the resulting cement giving tensile tests which are similar to those of Portland cement.

more important to ascertain the fineness of cement on a sieve of closer mesh, and in recent specifications a residue of 18 per cent. on a sieve having 180 × 180 meshes per square inch is common.

2. **Weight per Bushel.**—Portland cement is sometimes tested for the weight of a standard bushel, filled with the cement under definite conditions, the usual figures ranging from 108 to 115 lbs. per bushel. The object of this test is to detect underburnt cement, which is lighter and packs less closely than cement from well-burnt clinker. The test is not a good one, owing to the fact that the weight per bushel varies with the fineness of the cement apart from its quality in other respects. Thus, a cement leaving a residue of 10 per cent. on a 76 sieve will weigh about 108 to 110 lbs. per bushel, and one leaving 10 per cent. on a 50 sieve will weigh 114 to 116 lbs. per bushel. In consequence of this defect the test has been recognised as obsolete, and is now abandoned.

3. **Specific Gravity.**—Fresh, well-burnt Portland cement has a specific gravity of at least 3·15, and the specific gravity may be as high as 3·19. When aërated by exposure to air the specific gravity may fall to 3·10, underburnt cements falling below this. The test is a better criterion of quality than is the determination of the weight per bushel.

4. **Setting Time.**—Hydraulic cement varies greatly in setting time—from five minutes to several hours. The setting is generally retarded by aëration, for this slakes the calcium aluminate on which the initial setting depends (see *Cement*, Vol. II.). The setting of cement is ascertained by applying a standard "needle" —*i.e.*, a steel point of definite area loaded with a given weight. When the point ceases to make an impression, the cement is considered set. An apparatus for taking an autographic record of the setting time of cement has been devised.

5. **Tensile Strength.**—This is determined by gauging cement, either neat or mixed with a definite weight of standard sand * (usually three times the weight of the cement) with water to a stiff paste, and filling it into moulds of the shape shown at M in Fig. 1. The briquettes after the elapse of a definite period—*e.g.*, 3, 7, 14, or 28 days, during which they are kept in water—are broken in tension by a machine similar to that shown in Fig. 1, where A is a standard carrying a steelyard, F, from which is suspended a clip, B, below which a second clip, C, is attached to

* By standard sand is meant clean sharp washed sand of even size such that the sand will pass through specified sieves; in this country the sand must pass a sieve having 20 × 20 meshes per square inch, and be caught on one with 30 × 30 meshes per square inch.

a small horizontal hand wheel, R, serving for adjustment; the briquette, shaped in the mould, M, is held in these clips and load applied to it by traversing the weight, D, along the steelyard, this operation being performed at a uniform speed by means of the weight, W, and the dash-pot, P; this last consists of a cylinder filled with oil and fitted with a piston in which is a small hole, so that the movement of the piston as the weight falls is con-

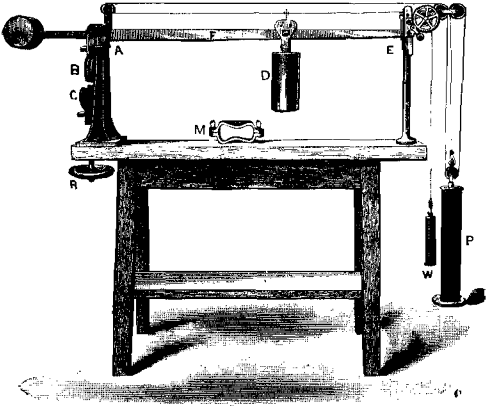


Fig. 1.—Machine for testing tensile strength of cement.

A, Standard; F, steelyard; B, C, clips; M, mould for briquette; D, travelling weight; W, falling weight; P, dash-pot; R, wheel for adjusting the clips; E, end of steelyard, with brake.

trolled by the slow passage of the oil from one side of the piston to the other. The waist of the briquette is of known size, usually 1 × 1 inch (= 1 square inch section) or 1½ × 1½ (= 2¼ square inch section).* The clips that hold the enlarged ends of the briquette are best lined with rubber blocks to prevent

fracture at the point in contact with them. The briquette is broken by the pull exerted by the lever of the testing machine as the weight is run out. Fracture occurs at or about the waist of the briquette, and the result is calculated from the area of the waist and from the breaking strain, and stated in lbs. per sq. in. An automatic brake is sometimes provided at the end of the steel-yard, E, which stops the weight, D, on the fracture of the briquette, and so avoids the need for constant attention on the part of the operator. A cement of good quality should have a tensile strength of at least 400 lbs. per sq. in. when tested neat at 7 days, or 250 lbs. per sq. in. when mixed with three times its weight of standard sand and tested at 28 days. Finely-ground cements will give a higher sand test.

6. **Soundness.**—A cement complying with the foregoing tests is not necessarily sound. An unsound cement sometimes appears sound for weeks after it has been used, and then expands and "blows," causing injury and destruction to the work in which it has been used. The soundness of cement is generally determined by observing the behaviour of a thin pat on a glass plate kept in water for twenty-eight days; it should neither crack nor buckle. Time can be saved and a more rigid scrutiny effected by one or other of the so-called "hot tests," in which the test pieces are kept at elevated temperatures, under definite conditions. Probably the best of these is the Le Chatelier test, by which the expansion of a small cylinder of cement heated to 100° C. is measured in a simple manner. It is officially used in France and in this country. Such tests, like others applicable to materials of construction generally, are best performed by experts rather than attempted by the user of the material, as he seldom possesses the requisite apparatus, knowledge, and experience; they should never be omitted for buildings of any importance.

STRUCTURAL METALS.

IRON.—Iron is used as cast iron for columns, pillars, bed-plates, frames, and standards of machinery, and as wrought iron and steel for girders, roofs, bridges, rails, boilers, and the moving parts of machinery. The production and varieties of cast iron are dealt with in the section on this material (see *Metallurgy*). The variety known as grey cast iron is that most frequently used for the production of castings, but mottled is employed when castings of special strength are required. The former has a uniform grey fracture in which the graphite can be seen; the latter is mottled in fracture, as its name implies.

The fusibility of cast iron is closely connected with the condition of the carbon which the metal contains (see *Iron*, in section on *Metallurgy*). Foundry pigs Nos. 1, 2, and 3 are grey irons, decreasing in content of graphite (and consequently in greyness of fracture), and also in fusibility, as the numbers rise. They increase in combined carbon, and consequently in hardness, in the same order. The medium quality of these three is the best for castings which are to possess considerable strength without undue brittleness. Good cast iron has a tensile strength of 7 tons per square inch, and a compressive strength of 40 tons per square inch. It is comparatively rigid and capable of little flexure or extension, and is, therefore, mainly used in compression. Where it is advantageous to have a hard wearing surface —*e.g.*, in tramway crossings, trolley wheels, or rollers—the casting is chilled by forming that part of the mould which corresponds with the portion to be chilled of massive metal, so that the cast iron is solidified rapidly and retains much combined carbon, thus acquiring extreme hardness.

Contrariwise, when it is required to confer softness and toughness on light cast iron articles of complex form, *malleable castings* are produced by imbedding the articles in hæmatite and heating them for some days. (For the *rationale* of this process see the section on *Metallurgy*.) The strength and reliability of cast iron depend upon its composition and the care and skill used in its casting. Analyses of a good foundry iron and of one containing more phosphorus and silicon, and therefore less strong but more fluid in casting, are given below.

	Foundry Iron No. 2.	Cleveland No. 3
Graphitic carbon,	2·68	3·70
Combined ,,	0·45	0·30
Silicon,	1·72	2·50
Manganese,	0·54	0·72
Phosphorus,	0·68	1·50
Sulphur,	0·04	0·04
Iron,	93·89	92·00

The specific gravity of ordinary grey cast iron is about 7·1.

With regard to these figures it may be said that if special strength be required the silicon should not exceed 2 per cent., nor the phosphorus 1 per cent. When intricate castings of small strength, but accurate outline, are to be made the amounts of

both silicon and phosphorus may be nearly doubled. It is better to remelt the iron that is to be used for castings than to tap it directly from the blast furnace. The remelting is conducted in a cupola, which is an upright cylindrical furnace provided with a blast and filled with mixed coke and pig, the iron settling as a liquid in what corresponds with the crucible of a blast furnace, and being tapped when the casting is to be made. During the remelting some of the silicon in the iron is oxidised and combines with the small quantity of lime added as a flux. At the same time a little sulphur is acquired by the iron from the fuel. Thus it happens that a soft iron is hardened by remelting, although this may be carried far enough to deteriorate the iron. The reason for the hardening which arises from the elimination of silicon, is explained in the article on Iron (see *Metallurgy*). The quality of cast iron is sometimes improved by the addition of aluminium to the iron in the ladle, the quantity used being about 0·2 per cent. of the weight of the iron. As regards the mechanical quality of castings, they should be free from scabs and blow holes, and in important work a portion of the metal should be cast separately, as a bar, and tested. Castings are often porous, and give evidence thereof in the case of hydraulic cylinders, which frequently weep when first taken into use. Slight leakage of this sort is automatically cured by the rusting of the pores. A good casting will ring sound when struck and have sharp clean edges and a uniform fine-grained grey fracture.

Wrought Iron (puddled iron) has been largely replaced by "mild steel," that is ingot iron (*q.v.*), for heavy structural purposes—*e.g.*, for bridges, rails, and girders—but it is still used where a tough weldable material, easily wrought by the smith, is required. Its content of the impurities characteristic of iron —viz., C, Si, S, P, Mn—is not now necessarily smaller than that of ingot iron, but it is sharply distinguished therefrom by the presence in it of slag from the puddling process (see *Metallurgy*) occurring as layers between the laminæ representing the original bars of iron welded together in the process of manufacture. On account of the presence of this slag wrought iron has a stratified structure easily seen at the fracture of a test piece. The best is grey and fibrous, though frequently patches of crystalline material exist throughout the section. Various grades of wrought iron are commercially known. Thus "puddled bar"—which is not fit for structural use because of the large amount of slag which it contains (rendering it locally weak) and its imperfect fibre—is the first product of the hammering and rolling of the puddled blooms (see *Puddling*). "Merchant bar" is that which

has been cut into lengths, piled and rolled into a new bar. The slag is thus expressed and the iron rendered more fibrous. Repetitions of this process yield "best bar," "best best," and "best best best bar." "Scrap bars" are made from short pieces welded and rolled together. If the scrap used is clean and of good quality, "best scrap" and "best best scrap" bars are produced. The valuation of wrought iron is effected by analysis and mechanical testing. The following analyses show the ultimate composition of commercial wrought iron :—

	South Staffordshire Wrought Iron.	Wrought-Iron Pipe.
Carbon,	0·06	0·027
Silicon,	0·04	0·200
Sulphur,	0·05	0·038
Phosphorus,	0·20	0·609
Manganese,	0·08	0·093
Iron (by difference),	99·57	99·033

In addition to these impurities there is generally present a considerable quantity of slag; this consists chiefly of oxide of iron. As much as 1 per cent. of slag may be present in ordinary wrought iron.

The influence of impurities upon wrought iron is similar to but smaller than that which they exert upon ingot iron, the reason for this difference being that in wrought iron the impurities are not dissolved uniformly in the unoxidised state throughout the metal, but are partly present as distinct segregations in an oxidised or slagged condition. The presence of this slag causes local weakness mechanically, but the iron itself is little affected. Thus, the amount of phosphorus shown in the first analysis given above would be most injurious in ingot iron, but is of little moment in wrought iron. Nevertheless, wrought irons containing much phosphorus—*e.g.*, 0·5 per cent.—have a higher strength than normal samples, but are lacking in ductility and toughness. Much sulphur—*e.g.*, 0·3 per cent.—has also a harmful effect, rendering the iron red-short. Silicon is present in only small proportion in wrought iron. Manganese is not intentionally added to wrought iron as it is to ingot iron, and is not often present in considerable amount. In the cases in which it occurs it tends to counteract the evil effect of sulphur. With regard to the mechanical testing of wrought iron, it may be taken that it has a tensile strength of from 22 to 25 tons per square inch, and an extension of about 26 per cent. on a length

of 10 inches; it has a compressive strength of 16 to 20 tons per square inch. These qualities are ascertained by means of a machine similar in principle to that described under cement testing. The test bar is gripped by its enlarged ends between wedge clips, and a pull from an hydraulic cylinder is applied, the pull being balanced by shifting a jockey weight along the steelyard of the testing machine. The position of the weight on the steelyard measures the pull requisite to effect the fracture of the specimen. In breaking a specimen of ductile material such as wrought iron, it is found that before fracture the test piece behaves as a viscous substance and flows, being drawn down uniformly until a contraction takes place at whatever point happens to be weakest, and fracture occurs. The elongation (extension) of the specimen which is thus caused is a measure of the ductility of the material. In judging this quality, regard must be had to the length of the specimen used, as it is found that of two test pieces of the same material differing in length, the shorter will give the higher percentage of elongation. Similarly, the thicker the test piece, *cæteris paribus*, the greater the percentage of elongation. The appearance of the test piece, before and after fracture, is shown in Fig. 2. The advantage

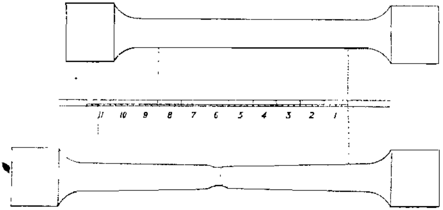


Fig. 2.—Appearance of test piece before and after fracture. (Wrought iron.)

of a ductile material such as wrought iron is that it will withstand shock, or even deformation, without sudden fracture. Those impurities which render the iron cold-short will decrease its ductility. A test frequently employed for determining toughness and ductility is the bending test, in which the test piece is bent over a bar of given radius, or even hammered down flat upon itself. The angle through which it can be bent before

fracture occurs at the bend is a measure of the ductility of the material. Ductile materials, when subjected to a gradually increasing load, as in a testing machine, carry the load up to a certain point with trifling increase of their length, and on the removal of the load return to their original dimensions. On further increasing the load, the material "breaks down"—*i.e.*, begins to stretch in more marked degree, and does not "come back" on removing the load. This point is known as the "elastic limit," or more properly "yield point," and is often much below the ultimate tensile strength. Thus the yield point of wrought iron having a tensile strength of 25 tons per square inch is about 13 tons. In considering the strength of materials for structural purposes, the yield point should be taken as a measure of their tenacity, and not the ultimate tensile strength. Ordinary practice is, however, the reverse of this. Thus the "factor of safety" of a structure is the ratio of the maximum working load to the ultimate breaking strain, whereas it would be more rational to state it in terms of the yield point of the material. For instance, a wrought-iron girder with an ultimate tensile strength of 25 tons is said to have a factor of safety of 5 when loaded with 5 tons in tension, whereas the real factor of safety is about 2·5 with this load.

Wrought iron (in common with other structural materials) has been found susceptible of change by the application of repeated alternating stresses well below its yield point. Such stresses occur in railway axles, piston-rods, and other moving parts of machinery, and may lead ultimately to the destruction of such parts. The change induced in this manner appears to be associated with a tendency of the originally fibrous material to become crystalline. The matter is, however, still the subject of investigation.

Ingot Iron and Mild Steel.—Since the device of the Bessemer and similar processes (*see section on Metallurgy*), iron containing from 0·08 to 0·6 per cent. of carbon has been prepared in ingot form and used for making girders, bridges, boiler plates, ships, rails, and steel castings. The milder grades, containing from 0·08 to 0·3 per cent. of carbon, are best termed **ingot iron**, as they lack the characteristic property of steel—viz., the capability of being hardened and tempered. The fact that manganese is used in the manufacture of these products involves the presence of this metal in the finished material and influences its hardness, manganese acting as a hardening agent in the same way as carbon, though in a smaller degree. The character of ingot iron and mild steel is best judged from its analysis; typical analyses are appended :—

	Very Mild Steel.	Mild Steel for Boiler Plates.	Bessemer Rail Steel.	Gun Steel.	Tool Steel.*
Carbon,	0·078	0·16	0·453	0·53	1·06
Silicon,	0·007	0·02	0·068	0·03	Nil.
Sulphur,	0·080	0·01	0·048	*Trace.*	0·02
Phosphorus,	0·047	0·06	0·050	0·01	0·03
Manganese,	0·698	..	0·882	..	0·33

It must be understood that these figures vary considerably with different samples, notably in the proportion of manganese, various quantities of which remain over after it has fulfilled its function in the process of manufacture. It may be taken as a rough guide that the sulphur and phosphorus in all ingot irons and steels should not exceed 0·05 per cent. The permissible limit varies, however, with the percentage of carbon: thus, although even this amount (0·05 per cent.) is most injurious to tool steel (with 1 per cent. carbon), a somewhat larger quantity (up to 0·08 per cent.) may be tolerated in ingot iron containing under 0·2 per cent. of carbon. Modern ingot iron, containing not more than 0·05 per cent. of sulphur or phosphorus and about 0·5 per cent. of manganese, will have a tensile strength of about 25 tons per square inch with 0·1 per cent. of carbon, 30 tons with 0·2 per cent., 35 tons with 0·3 per cent., and 40 tons with 0·4 per cent. The correspouding elongations on a length of 8 inches are 28, 24, 20, and 15 per cent. of the length of the specimen before fracture.

The fracture of a test piece of ingot iron or steel is distinguished from that of wrought iron by being perfectly homogeneous and silky in appearance, and free from any sign of lamination. Mild steel with a content of carbon of 0·4 per cent. has a specific gravity of about 7·89, while hard razor steel with 1·5 per cent. carbon has a specific gravity of 7·78. Steel castings, other than those of crucible cast steel, contain from 0·5 to 0·7 per cent. of carbon, and with regard to the remaining impurities are similar to ingot iron, save that 0·2 to 0·3 per cent. of silicon is sometimes added to aid in the production of a sound casting, and a portion of this remains in the finished metal. Unless subsequently forged, they are not so strong as would be rolled steel of the same composition.

Of late years several special qualities of steel containing small

* Inserted for the sake of comparison; such steel is not used for structural purposes, and is made by the cementation process (*q.v.*).

quantities of the less common metals have been brought into use. Thus *chromium steel* is made and used for railway tyres and for projectiles. A specimen containing 2·54 per cent. Cr and 0·39 per cent. C had a tensile strength of 44 tons per square inch and elastic limit of 24·5 tons, an elongation on 2 inches of 24·5 per cent., and a reduction of area of 33·8 per cent. Lately, chromium steel has been partly replaced by steel containing *tungsten*, *vanadium*, or *molybdenum*, but the behaviour of these steels in practice is not yet fully ascertained. Tungsten (and, to a smaller extent, molybdenum) is largely used for tool steels. The presence of 0·1 to 0·2 per cent. of vanadium is said to raise the elastic limit and tensile strength of mild steel by 50 per cent. or more. It also retards segregation and increases resistance to shock (*cf.* table, p. 35). Ingot iron to which aluminium has been added is not greatly different in tensile strength from ordinary wrought iron, but is said to be sounder. Thus a sample containing 0·38 per cent. Al and 0·15 per cent. C had a tensile strength of 26 tons per square inch, an elastic limit of 20 tons, an extension on 2 inches of 40·35 per cent., and a reduction of area of 60·74 per cent. Generally speaking, Al is added to ingot iron to reduce oxides and make the cast sound; it does not otherwise affect the strength of the metal. *Nickel steels* are considered under the heading *Nickel* (p. 27; also *cf.* table, p. 35).

An important modified steel is so-called *manganese steel*, more properly a manganese iron alloy, the general qualities of which are described in the section on *Metallurgy*. When containing 10 to 12 per cent. of manganese it has a tensile strength of about 63 tons, an elastic limit of 30 tons, and an extension of 38 to 45 per cent. For special steels, see also under *Steel*.

COPPER AND ITS ALLOYS.—Iron, on account of its strength and cheapness, is used wherever possible in building construction, but for certain purposes a different material is a necessity, and such needs are filled by copper and its alloys. In the boilers of locomotives the fire-box stays and plates are generally made of copper, and the boiler tubes of brass or copper. In some cases, however, mild steel is used throughout for plates and tubes. Another large use for copper and its alloys is found in steam pipes and ships' sheathing and fittings. Copper used as such for structural purposes is always of the grade known commercially as "tough pitch" (see *Metallurgy*). The chief impurities of commercial copper of this description are As, Sb, Pb, Bi, Fe, Ni, and O.

The following analyses are typical of modern locomotive copper, I. being that of an ordinary fire-box plate of soft tough copper, whilst II., representing a tube plate, and III., of a tube,

are specimens of harder coppers recently tried in engineering practice :—

	I. Per Cent.	II. Per Cent.	III. Per Cent.
Cu,	99·50	99·34	99·45
As,	0·10	0·42	0·31
Sb,	0·01	Trace.	Trace.
Pb,	0·15	0·08	0·05
Bi,	Trace.	Trace.	Trace.
Fe,	Trace.	Trace.	Trace.
Ni,	0·04	0·05	0·02
Ag,	Trace.	..	..
S,	Trace.	..	..
O,	0·15	0·13	0·13
	99·95	100·02	100·00

A copper such as the first will have a tensile strength of about 14 tons, with an extension of 40 per cent. on a length of 6 inches. The harder and more arsenical copper has a slightly higher tensile strength and rather smaller extension. Special alloys of Cu and Ni have been lately used for locomotive tubes.

The influence of impurities upon the tensile strength and ductility of copper depends upon the simultaneous presence of oxygen, which diminishes the deleterious influence of certain of the impurities in a marked manner. Thus, in the case of pure electrolytic copper free from oxygen, bismuth when added to the extent of 0·1 per cent. greatly lowers the tensile strength and ductility, from the formation of a fusible alloy which segregates from the bulk of the copper and destroys the homogeneity of its structure. Arsenic and antimony, which have but little effect upon pure electrolytic copper in quantities up to 1 per cent., have usually been considered injurious in copper containing oxygen, but, as shown by the examples above, at present many engineers consider the addition of arsenic (up to 0·5 per cent.) advantageous for such copper. Lead, sulphur, iron, and tin have a similar effect. Nickel appears, on the other hand, to have a hardening influence, but without causing undue brittleness. When the copper, as in fire-boxes, is exposed to mechanical wear, the presence of a hardening agent is not objectionable, provided the copper remains fairly ductile. Thus it happens that old locomotive fire-boxes with much larger amounts of impurities than those quoted above have often rendered good

service; one which had lasted twenty years and run 500.000 miles contained—

Cu,	98·70
Ag,	0·03
Au,	Trace.
Pb,	0·41
As,	0·37
Sb,	0·03
Bi,	0·04
Fe,	0·01
Ni,	0·30
O,	0·02 (?)
S,	0·01*

Further remarks upon the influence of impurities upon copper in other respects will be found in the chapter on metals. The specific gravity of tough pitch copper, rolled or hammered, is about 8·9, varying a little with the impurities which it contains.

Another important use for copper is the manufacture of steam pipes. Small sizes may be made from solid-drawn tubes,† and are reliable up to the point calculated from the tensile strength of the metal. Larger tubes, however, are generally made by brazing together the edges of a cylinder rolled up from a piece of sheet metal. Many accidents have occurred from the bursting of such pipes. Where the failure cannot be traced to an imperfect join, it appears to be due to an alteration of the metal, probably by absorption of oxygen and sulphur, caused by its exposure to the fire during brazing. The difficulty is sometimes met by grouping several smaller solid-drawn tubes, the united cross-section of which is equal to that of the single large tube which they replace.

Alloys of copper and zinc, known generally as **brass,** are much used as structural materials. They range in composition from 90 per cent. of copper and 10 per cent. of zinc (*red metal*) to 60 per cent. of copper and 40 per cent. of zinc (*yellow metal, Muntz metal*). The best quality of brass where strength and ductility are required, as for locomotive tubes, contains 70 per cent. copper, 29·5 zinc, 0·3 lead, the balance (0·2 per cent.)

* This and other published analyses of copper must be received with reserve; the analysis of commercial copper is a matter of some difficulty, and needs special knowledge and experience.

† Seamless tubes have been made electrolytically by the Elmore process, which consists in depositing copper upon a revolving mandrel while subjecting it to the pressure of an agate style, this being found to have a consolidating action. Such tubes are now also made by the Cowper-Coles process, in which the copper is deposited on a mandrel revolving at a very high speed (1,000 to 2,000 revolutions per minute), which does away with the necessity of using additional pressure.

being made up of traces of iron and other impurities. More than 70 per cent. of copper yields a somewhat soft alloy, while more than 30 per cent. of zinc gives one which is less ductile. A somewhat commoner brass is composed of 66 per cent. of copper and 33 per cent. of zinc. Brasses containing more than 62 per cent. of copper are workable cold, but cannot be rolled hot.

The ordinary method of ascertaining the quality of brass locomotive tubes consists in ascertaining their composition by analysis, and submitting them to the mechanical tests of flanging the end and of hammering them flat, and bending double the sheets thus produced; this should be effected without the formation of cracks. The tensile strength of brass castings is 11 tons per square inch, and of rolled sheet 16 tons per square inch. The specific gravity of brass containing 66 per cent. Cu and 33 per cent. Zn is 8·3. Brass of good quality is made from the purest copper and zinc that can be obtained, and contains no metal (save in traces) other than copper, zinc, and lead, the last named being present to the extent of less than 0·5 per cent. More than traces—*e.g.*, 0·05 per cent.—of arsenic are considered objectionable.

A special variety of brass used for sheathing ships is Muntz or yellow metal, containing 60 per cent. of copper and 40 per cent. of zinc: its specific gravity is 8·2 to 8·3. Since the copper in yellow metal falls below the limit given above for brass (62 per cent.), this alloy can be rolled hot. Its advantage for sheathing depends upon the fact that it is less corrodible than copper.

Gun-metal is the name applied to alloys of copper and tin ranging from 91 per cent. Cu and 9 per cent. Sn to 84 per cent. Cu and 16 per cent. Sn. A grade frequently used contains 87·5 per cent. Cu and 12·5 per cent. Sn. Small quantities (up to 2 per cent.) of lead and zinc are often added. Gun-metal is stronger than cast brass, having a tensile strength of 15 to 20 tons per square inch, and a compressive strength of about 50 tons per square inch. The 9 : 1 alloy has a specific gravity of 8·5. It is used for strong castings (being stronger than cast iron) for the more delicate parts of machinery, for cocks and the like where it is exposed to corrosion, and for bearings. In casting gun-metal there is a great tendency to segregation, especially when the casting is massive, and cools slowly. Nearly white crystals that have thus separated may be seen in the fracture of slowly cooled gun-metal. *Phosphor-bronze* is a gun-metal containing lead and phosphorus, the following being a typical composition:—Cu, 79·7 per cent.; Sn, 10·0 per cent.; Pb, 9·5 per cent.; P, 0·8 per cent. It is used for bearings, pump linings,

and other wearing parts. Many special bronzes are used for bearings. Such bearings are all called "brasses" in engineering parlance, whatever their composition: brass itself is, however, not suitable for bearings. A typical locomotive "brass" bearing, adopted after much experiment on a large American railway, contains—Cu, 76·8 per cent.; Sn, 8·0 per cent.; Pb, 15·0 per cent.: P, 0·2 per cent. The presence of the large quantity of lead is found to diminish the wear of the metal and the local heating of the journals.

Delta and Bull Metal.—Of late years brasses and bronzes have been made which are capable of being forged and rolled, and serve to replace ingot iron and mild steel for certain purposes where a strong metal not easily corroded is required. One use to which they have been put is the manufacture of ships' propellers. Delta metal is a ferruginous brass containing about 55 per cent. Cu, 43 per cent. Zn, 1 per cent. Fe, and traces of lead and phosphorus. Bull metal is an alloy of the same type. Both metals may be forged and rolled, and even extended in a plastic condition through a die to form rods or bars. When intended for such treatment, the ingot or bar to be worked is *cast in a chill, so as to prevent segregation. Metals of this class* have a tensile strength of about 18 tons per square inch when cast, and one of about 30 tons when rolled, with an elongation of 15 to 20 per cent. on 10 inches.

Aluminium bronze is an alloy of copper and aluminium containing up to 10 per cent. of the latter metal. It can be cast, forged, and rolled, and may replace mild steel for purposes *where corrosion is to be resisted and its cost is not prohibitory.* It has a high tensile strength. Thus, a 10 per cent. alloy (cast) has an ultimate tensile strength of about 40 tons per square inch, and the same metal when rolled an equally high tensile strength and an elongation of 30 per cent. Five per cent. aluminium bronze is well suited for the ignition tubes of gas engines. Aluminium brass castings containing 63 per cent. Cu, 33·3 per cent. Zn, 3·3 per cent. Al, 0·33 per cent. Si, were found to have a tensile strength of 31·4 tons, and an elongation of 0·4 per cent. A similar alloy rolled had a tensile strength of 37·8 tons, and an elongation of 9·7 per cent. Two per cent. aluminium brass can be used as ships' sheathing. In making aluminium bronze, repeated fusion and casting are necessary to obtain a homogeneous alloy. In spite of their merits, these aluminium alloys have not found any considerable application.

White Bearing Metals.—Besides the bronzes mentioned above as being used for bearing metals, many "white metals" are made, consisting of alloys of lead, tin, antimony, zinc, and copper.

Such mixtures are readily fusible, and are cast in the space round the journal to be supported. They are also used for lining "brasses" that have become worn. Thus, a form of **Babbitt's metal** has the composition—Pb, 40 per cent.; Sn, 45·5 per cent.; Sb, 13 per cent.; Cu, 1·5 per cent. That used on the London and North-Western Railway has the composition—Sn, 84·2 per cent.; Sb, 10·5 per cent.; Cu, 5·3 per cent. Another now largely employed contains—Pb, 80 per cent.; Sb, 15 per cent.; Sn, 5 per cent. Alloys of this class, though of no great tensile strength, are sufficiently strong in compression to carry the load of even a heavy bearing: their comparative plasticity renders them less liable than "brass" bearings to "seize" and heat, and the coefficient of friction is generally low.

N.B.—The various alloys are considered more fully in the metallurgical section of this volume (Part II.).

ALUMINIUM is at present but little used as a true structural material, though its employment in this direction is increasing. The commercially pure metal (99 per cent. Al) is white, not very lustrous, and easily dulled by exposure to air: the corrosion is, however, only superficial. When cast it has a tensile strength of 7 to 9 tons per square inch, with an extension on 4 inches of 15 to 20 per cent., though many specimens have a much smaller extension. After rolling, its tensile strength is increased to about 16 tons, with an extension of about 4 per cent. on a length of 4 inches. It is best worked warm, at about the temperature used for zinc. It is difficult to solder, and this property hinders its use for many purposes. The chief impurities of commercial aluminium are *iron*, *silicon*, and *sodium*. The first is said to be injurious, but the effect of silicon is rather to increase the tensile strength, while diminishing the elongation. Alloys of aluminium containing a small quantity of copper, silver, nickel, or titanium have a higher tensile strength than the pure metal. Thus the addition of 2 per cent. of copper raises the strength of rolled aluminium to 19·5 tons; alloys containing 2 to 3 per cent. of titanium have a tensile strength of 18 to 27 tons per square inch in forgings, and similar results have been obtained with nickel and zinc. On account of its lightness and good electrical conductivity (about 59 per cent. of that of copper), *it has been proposed to use aluminium for telegraph and telephone wires*; and a wire with a copper sheathing and aluminium core, having a conductivity of 69 per cent. of that of copper, has also been devised. Al and its light alloys are used in castings for the gear and engine cases of motor cars.

NICKEL is used alone as a structural material to a small extent, its employment being practically confined to making

culinary utensils and chemical apparatus. Its chief alloys are dealt with under *Nickel* in the section on *Metallurgy*. Nickel (98 to 99 per cent. pure) itself is not difficult to cast, but is cold-short. Cast bars are usually spongy, but after hammering become compact and tough. The addition of a very small quantity of magnesium removes occluded gases from nickel, and gives a metal free from blow-holes, the ductility and malleability also being improved. Aluminium may be substituted for magnesium, but an excess tends to make the nickel too hard. Nickel steels are now largely used for armour plates, guns, and naval purposes. Such steels contain 3 to 5 per cent. of nickel, steels with 3 per cent. Ni especially being largely used. Nickel steels with 3 per cent. Ni and 0·2 per cent. C have a tensile strength of 41 to 42 tons per square inch, an elastic limit of about 27 tons, an extension of 26 to 28 per cent. in 3 inches, and a reduction of area of 60 to 68 per cent. In general, the elastic limit of such steel is about the same as the tensile strength of ordinary mild steel, the elongation and reduction of area being about the same for both. The welding of nickel steel becomes more difficult with increasing percentages of nickel; with 3 per cent. nickel steel good results can be obtained, however, if care be taken. The tensile strength and elastic limit of nickel iron alloys and nickel steel increase regularly with the percentage of nickel up to about 20 per cent. of nickel, after which they decrease to some extent, the elongation increasing abnormally up to about 30 per cent. of nickel. The magnetic properties of a nickel iron alloy containing 25 per cent. of nickel are remarkable, the alloy being scarcely magnetic until cooled to − 40° C. (− 40° F.). It then becomes magnetisable and retains this property until heated to 600° C. (1,112° F.). Tests made on wire of this composition showed, before cooling, a tensile strength of about 50 tons per square inch, and an extension of about 30 per cent.; after cooling, a tensile strength of 85 tons, and an extension of 7 per cent. Rod or plate, containing 25 per cent. Ni, 0·27 per cent. C, and 0·85 per cent. Mn, had, in the uncooled state, a tensile strength of 46 tons per square inch, an elastic limit of 13 tons, an extension of 29 per cent. in 8 inches, and a reduction of area of 29 per cent. (*cf.* table, p. 35). The corrosion of nickel steel and other nickel alloys is considered on p. 49.

Monel Metal.—Attention has been called to this alloy recently by its use in the sheet form in the roof of the new Pennsylvanian Railway Station in New York. The sheets are fastened with nails of the same alloy. It consists of Ni 70 per cent., Cu 30 per cent., and is smelted and refined directly from the Ni-Cu matte produced from ores of the Sudbury district in Canada. Monel

metal has a higher tensile strength than Ni steel. Its hardness makes it more difficult to roll than steel sheets. It resists corrosion, takes a fine polish, and possesses many of the properties of metallic nickel.

ROOFING MATERIALS.

The chief roofing materials in common use are slates, tiles, sheet lead, sheet zinc, zinced ("galvanised") iron, and tinned iron (tin-plate).

SLATE is an argillaceous rock which is of sedimentary origin, and has had cleavage planes developed in it, its peculiar fissile character (slaty cleavage) being due to a re-arrangement of the particles of the rock consequent on compression. Slate generally consists essentially of aluminium silicate, coloured with ferrous oxide. Light coloured slates are sometimes found; dead black slates are rare. Iron sulphide is often present both as pyrites and marcasite. The former is not injurious, but the latter causes disintegration of the slate on account of the ease with which it is oxidised by weathering. Calcareous slates, containing as much as 49 per cent. of calcium carbonate are also found. A slate of good quality should have a fine grain, should ring sharply when struck, and should not be easily scratched by the finger nail. Its colour does not serve as a criterion of quality. The most important property, besides toughness, to be considered in judging slate, is its degree of porosity. It should be as nearly non-absorbent as possible. The difference in quality of slates in this respect is shown by the fact that the volume of the pores of the slate varies from 0·05 to 6 per cent. of the apparent volume of the whole slate. Many commercial varieties of slate are distinguished. The Welsh are considered the best, and of these the Silurian are better than the Cambrian slates, for they are less siliceous than the latter, and more easily cleaved. The sizes most in use for roofing are distinguished by fancy names—*e.g.*, "wide viscountesses," "small ladies," etc., the enumeration of which cannot be attempted here.

Certain calcareous sandstones—*e.g.*, **Stonesfield slates,** which are not true slates—are used for ornamental roofing, but, being comparatively thick, their weight is against their general employment. Slate is an excellent roofing material, but is somewhat costly, and on account of its usually dark colour absorbs much heat when exposed to the direct rays of the sun, thus failing to keep the building beneath cool.

TILES are made by moulding and burning brick clay; their manufacture is described in the chapter on *Clay Industries*,

Vol. II. They are thicker, heavier, and more porous than slates. For tiles to be efficient they must fulfil one of two conditions. Either they must be of open porous structure, so that water soaking in may be able on freezing to expand without splitting the tile, or they must be burnt at a clinkering temperature, and be as dense and non-porous as stoneware or biscuit porcelain (*q.v.*), so that water cannot find its way in. The same end may be attained by soaking porous tiles in tar. Glazed tiles with a porous body are of little use, as the least imperfection in the glaze permits the entrance of water, which in expanding by freezing in cold weather causes the glaze to scale off. Dense clinkered tiles can be glazed without this result, but in this case the glaze is of small utility save as giving a smooth surface upon which lichens cannot grow.

ZINCED IRON (*galvanised iron*) is largely used as a roofing material, and also for the entire construction of sheds and other cheap and temporary structures. The process of "galvanising" consists in removing the scale from the plates and other articles (a preliminary annealing being performed in the case of plates) by pickling in hydrochloric acid, washing, scouring with sand, and passing through a bath of melted zinc which is covered with ammonium chloride. The latter serves as a flux, and induces the coating of the iron by the zinc. For galvanised sheet, a little tin (2 to 3 per cent.) is added to the bath, and produces large crystalline spangles on the finished goods, which appearance is often erroneously taken as a proof of good quality. A small quantity of aluminium—about 0·01 per cent.—is often added to the zinc bath to reduce any zinc oxide that may be diffused through the metal. The plates are generally brought out between rollers or brushes to economise zinc, the proportion of which adhering to the iron is usually reckoned in ounces per square foot, 2 ounces being a good average coating. Zinced sheet is often corrugated to increase its strength and prevent it from buckling when used for walls and roofs. A considerable proportion of iron passes into the galvanising bath and sinks to the bottom as a zinc-iron alloy. This hard zinc, containing about 5 per cent. of iron, is removed and liquated from time to time. As the iron of the tank is also dissolved by the zinc—resulting in the ultimate destruction of the tank—attempts have been made to avoid contact of the zinc with the tank by allowing the zinc to float on a layer of melted lead (to protect the bottom), and by lining the sides of the tank with fire brick. The acid pickling bath used to clean the plates, etc., may not legally be turned into sewers or rivers, and is apt to become a nuisance. It contains about 10 per cent. of iron as ferrous chloride, and but little free acid. An attempt at its

utilisation has been made by Turner, who allows the liquor to trickle into a furnace, where the liquid evaporates and the ferrous chloride is decomposed in accordance with the equation $2FeCl_2 + 2H_2O + O = Fe_2O_3 + 4HCl$. The hydrochloric acid is condensed by the usual means (see *Salt-cake*, Vol. II.), and re-used. The ferric oxide serves as fettling in puddling furnaces. Most grades of cast iron, wrought iron, ingot iron and steel, and articles of the most diverse shape may be zinced, but certain differences in facility are observed. Thus cast iron is least easy to zinc; wrought iron, ingot iron, and mild steel take the metal readily; but hard steel—*e.g.*, wire for ropes—is less readily coated. The high temperature of the galvanising bath (420° C. = 788° F.) also affects the temper of hard steel wire, diminishing its tensile strength. The fact that zinc forms an alloy of low strength on the surface of the iron, immediately beneath the visible coating, appreciably impairs the strength of goods of light section—*e.g.*, wire and small chains. Recently, iron articles have been galvanised in the cold by immersing them in a neutral solution of zinc sulphate through which an electric current of 20 to 70 amperes per square foot is passed. In this case, the zinc merely plates the iron without forming an alloy with it. Still more recently, a process due to Cowper-Coles, and known as *Sherardising*, has been introduced. It consists in placing the cleaned iron articles in a rotating drum, or other movable metallic receptacle, together with zinc dust, or a mixture of finely-divided zinc and oxide, and about 3 per cent. of carbon. The whole is heated to dull redness for a period depending on the thickness of coating required. The coating obtained is distinguished by its silver grey tint. A still later modification of the process is that known as "vapour galvanising," in which the articles are placed either in a separate chamber filled with zinc vapour, or above molten zinc. In either case it is necessary to move the objects to ensure an even coating. Iron is sometimes coated with lead instead of zinc. The general method of procedure is the same, but even greater care must be bestowed on the preparation and cleaning of the iron to be leaded, as lead adheres less readily than zinc. The cheapness of lead (£13 per ton, as compared with £23 per ton for zinc *) gives it an advantage, as does its indifference to acids and its ductility, which prevents it from tending to scale when the article coated with it is bent. It does not impair the strength of the iron or steel to which it is applied, and the risk of softening hard steel wire (referred to above in the case of zinc) is much lessened, as the fusing point of lead is

* Prices of all metals fluctuate considerably.

only 325° C. = 617° F. Against these properties must be set the inferiority of its protective action to that of zinc (*v.i.*), and its toxic qualities, which make it unsuitable for lining cisterns and pipes which are used for holding and conveying water. If used in the same thicknesses as zinc, it increases the weight of the coated article, on account of the difference between the specific gravity of lead (11·4) and that of zinc (6·9). The advantage in point of cost mentioned above is, therefore, less than appears from the comparison of the prices per ton of the two metals.

TINNED IRON (*tin plate*) is not much used as a structural material (save occasionally for roofs, for which it is ill adapted), but is conveniently considered here on account of its analogies to and differeuces from zinced plate. It is used for small hollow ware, and inasmuch as it can be cheaply soldered and made up, it is not ousted by zinced iron in spite of the low price of zinc compared with that of tin. The process of manufacture is as follows :—Heated bars of wrought iron or ingot iron are rolled to a plate, which is folded across the middle, again heated and rolled. The doubling and rolling are repeated until as many as thirty-two thicknesses have been rolled. The edges of this compound plate are sheared off, and the individual plates split asunder. The coating of iron scale which forms during the rolling prevents the plates from welding together. The plates are then pickled in dilute sulphuric acid,* scoured, and annealed. The surface is then improved by cold rolling, which renders a second annealing necessary. After a second pickling in a more dilute acid, the plates are passed into the "grease-pot," containing melted tallow or palm oil. They are then dipped in the tin bath, the metal in which is covered, to prevent oxidation, with grease or zinc chloride. To perfect the coating of tin, passage through several successive tin pots follows. By this systematic working, the preliminary coating is done by the most impure bath, and the final layer put on in a pot of nearly pure tin. To squeeze off the excess of tin, the plate is finally passed through rollers running in a grease bath. Although tin plate has a layer of tin-iron alloy intermediate between the iron plate and the tin coating proper, yet the diminution in strength due to this layer is less marked than in the case of zinced iron (p. 31). Thus it happens that thinner plate and wire can be tinned than can be zinced without injury.

* Pickling any light iron article in acid so as to cause the evolution of hydrogen at its surface renders it brittle by absorption of hydrogen ; this brittleness is removed on heating.

STRENGTH, PERMANENCY, AND PRESERVATION OF MATERIALS.

STRENGTH OF STRUCTURAL MATERIALS.—In the preceding sections the strength of ordinary metals used in construction has been incidentally given as a criterion of their quality. In the appended tables their values are compared with the corresponding figures for other materials. In general the mechanical property, the possession of which causes the choice of the material for its ordinary functions, is given, sometimes to the exclusion of its other less important mechanical properties.

The following figures refer to the mechanical properties of metals at the ordinary temperature—*e.g.*, at 15° C. = 59° F. At higher temperatures—*e.g.*, 300° to 400° F. (= 149° to 204° C.)—their tensile strength is generally greatly reduced, a matter of much importance in structures carrying heavy loads at high

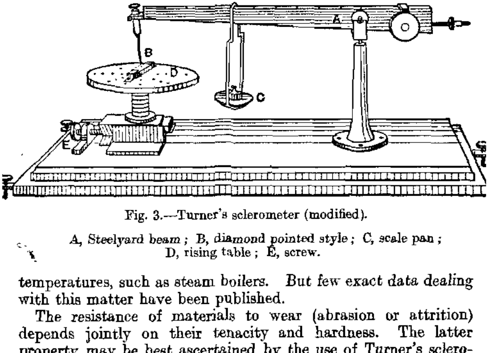


Fig. 3.—Turner's sclerometer (modified).

A, Steelyard beam; B, diamond pointed style; C, scale pan; D, rising table; E, screw.

temperatures, such as steam boilers. But few exact data dealing with this matter have been published.

The resistance of materials to wear (abrasion or attrition) depends jointly on their tenacity and hardness. The latter property may be best ascertained by the use of Turner's sclerometer (hardness measurer), a modified form of which, devised by one of the authors, is shown in the figure above. A steelyard beam, A, swings on a pivot in a horizontal plane, and oscillates on knife edges in a vertical plane. At the end remote from the knife edges is a style, B, shod with a diamond point. This style is set at an angle with the plane of the beam for a purpose which will be explained later. A scale pan, C, slides

STONE, BRICK, CONCRETE, AND CEMENT.

Name.	*Compressive* Strength. Tons per Square Foot.	Tensile Strength. Lbs. per Square Inch.	*Weight* per Cubic Foot. Lbs.	Percentage of Water absorbed. Reckoned on Weight of Stone.
STONE—Sandstones—				
Prudham,	455·3	..	142·5	4·00
Craigleith,	352·8	453	..	3·2
Granites—				
Rubislaw (Aberdeen),*	1098·8	..	163·7	0·09
Kenmay (Aberdeen),†	1211·1	..	161·0	0·21
Aberdeen (another),	1800	..	164·1	0·16
Cornish,	1402	..	164·5	0·41
Norwegian,	1870	..	165·5	0·34
Whinstone,	769·0	1469	170·0	0·10
Calcareous Stones—				
Oolitic limestone (Portland)	287·0	..	137·6	6·84
Dolomitic „ (Anston),‡	301·9	..	132·2	7·50
True dolomite,	577·4	..	145·4	4·62
Marble (White Italian),	1400	722	170	Trace.
Marble (Red Devon),	476·6	..	..	..
BRICK—				
London stock,	128	..	..	..
Gault brick,	135·4	..	..	19
Staffordshire blue brick,	267·8	..	..	3·7
Red brick (machine made),	113·8	..	..	9·9
Spent lime and clinker,	361	..	..	6·0
CONCRETE—				
1 cement : 6 ballast (twelve months old),	91	..	..	..
1 cement : 2 ballast,	160	..	..	..
CEMENT—				
A. NEAT—				
7 days,	576	..	..	..
3 months,	739	..	..	..
6 „	771	..	..	..
12 „	932	..	..	..
24 „	..	..	..	..
3 sand : 1 cement—				
7 days,	275	300	..	..
3 months,	308	350	..	..
6 „	360	400	..	..
12 „	360	425	..	..
24 „	..	450	..	..
B. NEAT—				
7 days,	488	611	..	..
28 „	598	869	..	..
3 sand : 1 cement—				
7 days,	143	233	..	..
28 „	208	290	..	..

* Used for London Bridge. † Used for Forth Bridge.

‡ Houses of Parliament.

METALS.

Name.	Tensile Strength. Tons per Sq. Inch.	Elastic Limit.	Extension. Per Cent.	Reduct of Are Per Ce
Cast iron,	7	2	*Inappreciable*	*Inapprec*
Malleable cast iron,	17·8	...	5·6	6·9
Wrought iron,	22-25	13-15	26	30-40
Ingot iron (0·1 per cent. C),	25	15	28	50
,, (0·2 ,, C),	28	17	24	40
,, (0·3 ,, C),	35	21	20	30
,, (0·4 ,, C),	40	24	15	25
Cast steel hard (0·6 per cent. C),	60	...	1	...
Hard steel wire (fine gauge),	100	...	1	...
Bull-headed railway rails,	38-45	...	15	...
Tramway rails and fishplates,	40	...	12 in 2″	...
Locomotive tyres,	48-54	...	15·11 in 2″	...
,, axles,	32-37	...	25 in 3″	...
Carriage and wagon tyres,	40-42	...	20 in 2″	...
,, ,, axles,	26-30	...	30 in 3″	...
*Forged iron, annealed (99·80 Fe, 0·08 C),	18	9	52 in 2″	76
* ,, nickel, ,, (98·80 Ni, 0·16 C),	13¼	7	54 in 2″	52½
*Nickel steel (3 p.c. Ni, 0·2 p.c. C),	42	27	26 in 3″	61
,, (3·82 p.c. Ni, 0·19 C, 0·65 Mn),	33	25	35 in 2″	55
,, (15·48 p.c. Ni, 0·23 C, 0·93 Mn),	68	...	1 in 2″	1
Nickel iron (24·51 p.c. Ni, 0·16 C, 4·00 Mn),	78	25	14 in 2″	8
Nickel steel wire (27·8 p.c. Ni, 0·4 C),	80	...	6·25 in 2″	16·5
Nickel, rolled,	35	...	10 in 2″	...
Nickel, wrought, annealed,	42·4	...	23 in 2″	...
†Crucible steel (C, Mn),	27	16	35 in 2″	60
,, (plus 1 per cent. Cr),	38	25	30 in 2″	57
,, (plus 0·1 per cent. V),	35	28·5	31 in 2″	60
,, (plus 0·25 ,,),	39	34·1	24 in 2″	59
,, (plus 1 p.c. Cr + 0·25 V),	60·4	49·4	18·5 in 2″	46·3
Open-hearth steel (C, Mn),	32·2	17·7	34 in 2″	52·6
,, (+ 1 p.c. Cr + 0·15 p.c. V),	52·6	34·4	25 in 2″	55·5
Copper (tough pitch),	13-15	6·8	40	40
Brass (2 copper : 1 zinc),	15	...	...	...
Gun-metal (9 Cu : 1 Sn),	15-20	...	...	...
Phosphor-bronze, rolled,	32	Occasionally none. Sometimes 24 or higher.	18	50
,, ,, cast,	*18*	*12*	*11*	*10*
Muntz metal sheet,	21	...	50 in 5″	56
,, ,,	20	...	40 in 5″	48
Delta metal, cast,	32	16	18	20
,, rolled,	45	20	20	22
Bull metal, rolled,	36	21	10	15
,, cast,	24	16	10	15
Manganese bronze, cast,	30	15	28	20
Aluminium bronze (10 per cent.), rolled,	40	...	30	...
Aluminium, cast,	5	2·5	3	5
,, rolled,	16	...	4	...
Nickel,	85	...	...	...
Zinc, sheet,	7	...	...	...
Lead,	1	...	...	...

* Hadfield (*Proc. Inst. Civ. Eng.*, cxxxviii).

along the beam, which is graduated, and by its means a load varying from 1 to 100 grammes can be placed upon the diamond point. The piece to be tested is prepared with a polished surface free from scratches, and is clamped on the rising table, D. The diamond point is loaded with a known pressure and drawn across the polished surface. The style carrying it is sloped, as mentioned above, to prevent "chatter." By means of the screw, E, the table is moved bodily a short distance—*e.g.*, $\frac{1}{50}$ inch —and another trial made with a different load. The load which just suffices to abrade the surface of the specimen is a measure of its hardness. The instrument is preferably used in conjunction with a low-power microscope (1 inch objective) to view the scratches and decide which corresponds with the abrading load. The following table (*Turner*) shows the hardness of various materials, the figures being the load in grammes required to just scratch the specimen when tested by the sclerometer :—

Steatite,	1
Lead (coml.),	1
Tin ,,	2·5
Rock salt,	4
Zinc (annealed),	6
Copper ,,	8
Calcite,	12
Softest iron,	15
Fluor spar,	19
Mild steel,	21
Tyre ,,	20-24
Apatite,	34
Hard cast scrap,	36
Window glass,	60
Hardest chilled iron,	72

In choosing a material of construction in respect of its strength as distinct from its durability, it may be said that where static compressive loads have to be borne, a rigid material, such as stone, concrete, or such metals as are hard, and have a high compressive strength in the cast state (*e.g.*, cast iron and gun-metal), is preferable. When dynamic stresses have to be resisted, and toughness as distinct from rigidity is a necessity, some form of wrought metal, such as wrought iron, ingot iron, copper, brass, and special copper alloys (*e.g.*, phosphor-bronze), is employed. The tendency of most cast metals, if allowed to cool slowly, is to assume a crystalline structure favourable to rigidity and compressive strength rather than to toughness and tensile strength. By working—*e.g.*, rolling or forging—the crystals are commonly deformed in a longitudinal direction, and the metal acquires a higher tensile strength and ductility, with some loss of rigidity. Thus, as mentioned under iron, the cast metal is used for bed

plates and standards, and wrought or ingot iron for moving parts. The use of ingot iron or mild steel for rails is no exception to the rule, as the stresses to which a rail is subjected are eminently dynamic.

PERMANENCY OF STRUCTURAL MATERIALS.—The permanency of building materials depends jointly on their inherent powers of resisting the destructive agents to which they may be exposed, and on the character of their environment, which may aid or hinder the disintegrating and corroding effect of such destructive agents. These destructive agents may be divided into two classes, mechanical and chemical, the former being the more important.

Under the first head are included such influences as erosion by sand mechanically driven against the building by the wind, and the attack of rain and frost. With regard to the effect of sand it is obvious that it is likely to occur in places where the soil is loose and siliceous and the wind often high. Thus buildings on the sea coast are especially liable to this form of attack, and the side of a given building facing the quarter from which the prevailing wind blows, naturally suffers most. The effect of rain and frost is similarly localised by the action of the prevailing wind. The wind forces the rain into the stone, but, at the same time, causes the evaporation of the moisture when the rain has ceased; this will not, however, compensate for the increase of the action of acids which may have been carried in by the rain (see *Chemical corrosive agents*). Thus it comes about that the most exposed side of a building suffers most from weathering. Probably the greatest mechanical effect is brought about by frost, which tends to disintegrate the stone by the expansion, in the act of freezing, of the water enclosed in the pores, with consequent separation of particles of the stone. Cold alone, if the stone be dry, has no deleterious effect, whence it follows that stone as quarried and containing much moisture must be rendered fit for building purposes by being " seasoned "—*i.e.*, allowed to dry. The amount of water which a stone will absorb under its conditions of use depends on its texture, a loose, porous structure causing a large absorption. Even where the new stone does not absorb much water, it may tend to do so after use, if the grains composing it be easily removed by the mechanical action of wind referred to above, and its superficial structure thus rendered more porous. The capability of the stone to resist the action of frost is ascertained by a direct freezing test. The test piece is saturated with water and alternately frozen and thawed (a dozen times or more), and the loss of weight of the block by exfoliation determined. A test formerly much

in vogue (Brard's test), which consists in soaking the stone in a saturated solution of sodium sulphate, allowing the salt to crystallise in its pores, and repeating the operation, is fallacious, as the solution of sodium sulphate contracts in solidifying, and the expansion of water in the act of freezing is not imitated. The determination of the maximum amount of water which a stone will absorb is effected by soaking a test piece of known dimensions and weight until it is saturated, and ascertaining the increase of weight caused by the water which it has taken up. In the case of slate similarly tested, diphenylamine (M.P. 54° C. = 129° F., B.P. 310° C. = 590° F.) has been recommended. The behaviour of different classes of stones (and of bricks) with regard to the action of frost, may be thus generalised :—

(1) Those which are impermeable to moisture must plainly be unaffected. Such are stones of extremely close structure—*e.g.*, granite, and bricks and tiles burnt at a clinkering temperature.

(2) Those which are porous but are of open texture and fair cohesion are likely to suffer little, as although water finds its way into them, yet there is room for it to expand on freezing without causing disintegration.

(3) Those which are not very porous but are still hygroscopic, such as certain argillaceous varieties, are liable to serious attack, as water finds its way in and freezes in the pores without having room to expand.

The only satisfactory manner of determining the frost-resisting power of a stone is to submit it to the freezing test above-mentioned.

Although the foregoing paragraphs have dealt chiefly with the behaviour of stone, they apply equally to artificial stone, including brick and concrete. The latter have, however, certain defects of their own. Thus, bricks which have been made from clay containing alkali salts are liable to efflorescence, the salts (sodium sulphate and carbonate) appearing on the surface of the brick with a disfiguring effect. Other causes of the presence of soluble salts inducing efflorescence, are the presence of iron pyrites in the clay, and of sulphur in the fuel used to burn the bricks ; both these give rise to sulphuric acid during the burning, and the alkalies and alkaline earths present in the clay are converted into sulphates. Pyritic clay should, therefore, be avoided. Similar efflorescence occurs with artificial stone which has been made by a process involving the use of an alkaline silicate, as any residual alkali left after the washing process which the stones undergo, is gradually converted into carbonate, and appears upon the surface. Concrete and cement mortar may also give efflorescences of calcium hydroxide and carbonate, and, if in

contact with sea water, may develop growths composed chiefly of magnesium hydroxide, due to the interaction of the magnesium salts of the sea-water and the lime compounds of the concrete. The foregoing efflorescences are sometimes fairly harmless; frequently, however, they tend to cause damp places on the structure, destructive of paint and plaster, and even leading to the detachment of fragments of the wall. In the case of concrete these efflorescences owe their injurious character to the chemical actions involved rather than to any mechanical effect which they exert. They will be dealt with more fully in the next section.

The growth of lichens on stone and brick influences the permanency of these materials in a manner depending on the prevailing conditions. Thus, such a growth may serve as a protection from rain, but, on the other hand, may prevent the surface from drying. Since the plant needs a foothold, a smooth surface will be less able to afford support than a rough one. Porous brick and tile are typical materials upon which such growths occur.

In the case of metals, the possibility of mechanical destruction is less imminent than with stone and brick, on account of their closeness of grain and the fact that they are less frequently used than stone or brick for outside work, or if so used are protected by some external envelope. There is, however, one cause of failure (previously adverted to incidentally) which must not be overlooked in designing and maintaining metallic structures. It has been found that the frequent application of a load, well below that which the metal if tested in the ordinary way is found to be easily capable of bearing, eventually produces "fatigue" in the metal, tending to change its structure and causing it to become crystalline and brittle. It may be supposed that repeated agitation allows the molecules of the metal to assume the positions corresponding with the form in which it crystallises, and the consequent alteration to a less interlocking structure naturally decreases the strength of the material. Instances of the change in question are afforded by the failure of railway axles, which have been found to become crystalline after long use, and by the sudden snapping of brass chains, such as are used to support gas pendants, and are, therefore, subjected to repeated strains from the oscillation of the burners depending from them.

The use of many structural materials involves operations which have a considerable effect upon the permanency of the structure. This influence is distinct from that exerted by the quality of the materials of construction themselves. All methods

of uniting separate pieces of the same material, or of one material with another, come into this category and may be considered here.

The best method of joining is that of **autogenous soldering**—*i.e.*, the union of two pieces of the same material by bringing together the parts to be joined in a liquid or semi-liquid state. The process known *par excellence* as autogenous soldering is **lead-burning** (see *Vitriol*, Vol. II.). The operation of lead-burning consists in applying two clean surfaces of lead to each other and fusing their opposing edges, so that the molten metal forms a seam between the two, continuous and homogeneous with the portions joined. Fusion is effected by the flame of a blowpipe fed with hydrogen and air, the source of heat being sufficiently intense to fuse the metal locally without beating the adjacent portions, and being also clean and free from products of combustion (*e.g.*, sulphurous gases) capable of tarnishing the metal to be joined.* Another case of strictly autogenous soldering is afforded by the **welding** of iron and of steel. Here the metal is not actually fused so that it will intermix by its own flow, but when in a plastic state it is caused to flow by pressure, applied either as a steady stress or by hammering. The simplest form of welding is that practised by the smith, and consists in raising the temperature of the parts to be welded to a "welding heat"—*i.e.*, nearly the highest temperature of the forge (see *Industrial Temperatures*, p. 114), cleaning the surface by slagging (*fluxing*) off the oxide with sand or borax (which thus serves as a *flux*), and hammering together the surfaces to be joined. Wrought iron will stand a high welding temperature, and is correspondingly easy to weld. Ingot iron and mild steel are somewhat less easy to weld, and are worked at a rather lower temperature; higher carbon steel needs a still lower temperature and more careful working, borax and sal-ammoniac being used as fluxes, as a slag formed by the aid of sand is not sufficiently fusible at a red heat. A neat application of the use of a flux to be placed between the surfaces to be welded has been devised, and consists in employing fine soft iron-wire gauze, the meshes of which are filled with borax glass (fused borax). Pieces of this are placed between the metal to be welded, and present the flux at the precise spot where it is needed. The difficulty of welding high carbon steel is increased when it has to be welded to ingot iron or wrought iron, as a temperature suitable for the former is too low for the satisfactory working of the latter. Certain tools—*e.g.*, hack-saws,

* The strength and permanence of concrete made *in situ* and built up to form what is in essence a monolith, are largely due to the method of jointing, which is quite comparable with autogenous soldering.

vices, and hammers that need a hard working face and a soft, tough backing—are produced by welding hard steel to softer steel or iron. A skate blade and a compound armour plate are examples of the same practice. A difficulty which stood in the way of oxyhydrogen blowpipe welding—viz., the economical production of the two gases—has now been overcome by a method depending on the electrolysis of water (p. 96). The blowpipe, in which the gases are burned, is a conical mixed jet pipe with a small brass nozzle, and is now used for the autogenous soldering of iron, steel, copper, and other metals. Oxygen and hydrogen are used in the apparatus in the proportion of one to six respectively, and, as the decomposition process yields the two gases in the proportion of one to two the excess of oxygen is compressed into cylinders and sold for medical and other purposes. The use of oxygen and acetylene in a special blowpipe for supplying the heat necessary in autogenous welding is a recent development, and has many advantages. The oxygen is contained in a cylinder in a state of compression, while the acetylene is drawn directly from a generator of any ordinary pattern which yields the gas in a pure state and uncontaminated with air. The best welding results are obtained by a mixture of 1 volume of acetylene and 1·7 volumes of oxygen. The temperature of the flame (about 6,000° F. = 3,300° C.) is above that at which hydrogen will combine with oxygen to form water, and can only be exceeded by that found in a powerful electric furnace. The flame consists almost entirely of carbon monoxide, which is being converted at the extremity of the flame into carbon dioxide. The hydrogen dissociated from the acetylene remains temporarily in the free state, and forms a relatively cool jacket round the flame, protecting the inner zone from loss of heat, and at the same time excluding the possibility of oxidation, which is a difficulty met with in the oxyhydrogen process. Oxy-acetylene autogenous welding is applicable to a great variety of work, and its use is rapidly extending in engineering work generally. A recent method of welding which has found considerable employment is that depending on the use of electricity as a source of intense and local heat. A current of large quantity and low pressure, which may be obtained from an ordinary dynamo by the interposition of a step-down transformer,* is passed through the bars (or other pieces of iron) to be welded. At the point where they touch, the resistance due to their imperfect contact causes the transformation of electrical energy into heat;

* A transformer is the modern equivalent of an induction coil: a step-up transformer is essentially an induction coil; a step-down transformer a reversed induction coil.

as heating proceeds the resistance rises, in accordance with the general behaviour of metallic conductors, and more heat is generated, the opposed ends of the bars quickly reaching a welding temperature. During the process they are pressed together in the direction of their length, and the joint is finished by hammering in the usual way. An alternative method, applicable when it is not possible to make the two pieces of metal to be joined act as both electrodes, consists in the use of one as an electrode, and a carbon rod as the other electrode, local heating by means of the arc thus produced being engendered, and welding of the two pieces of metal effected. This method has also been applied to lead-burning. Electric brazing is also practised. The chief advantages of electrical welding are its rapidity and cleanliness, and the ease with which massive pieces of metal may be welded when already in place. Probably on account of the extremely local heating of the welded joint, an electrical weld is not as tough and reliable as a good hand weld, which can, when made in wrought iron, be bent through an angle of 180° cold, whereas an electrical weld usually fails at about 135°. Electrical welding, on account of the high and local temperature at command, can be applied to other metals than iron. Copper can be welded to copper, aluminium to aluminium, and indeed most metals to themselves and to each other. In these cases the joint is made by local fusion rather than by welding in the ordinary sense. A similar weld is obtained by the use of Goldschmidt's **thermite** process, in which the intense heat developed by the oxidation of aluminium at the expense of another metallic oxide, mostly ferric oxide, is utilised. The thermite, consisting of an intimate mixture of aluminium powder and ferric oxide, is fired by means of a fuse of magnesium ribbon, one end of which is embedded in a small ball of aluminium powder and barium peroxide placed in the thermite. The heat of the reaction produced is sufficient to melt the mixture, which is then poured on to the metal to be welded, the two pieces to be joined—*e.g.*, tram-rails—being clamped together and surrounded by a rough mould of sand. The weld is finished off by filing away, if necessary, the iron from the mixture which has fused on to the metal. In the case of rails, however, only the top surface is finished in this way, the lump of iron at the bottom being left, as it increases the strength of the joint. Autogenous soldering, using the phrase in its widest sense, has the advantage over other methods of joining that risk of destruction by the formation of galvanic couples from the contact of different metals with each other is minimised.

Methods of **soldering**, as distinct from autogenous soldering,

consist in joining two metals by an alloy more fusible than either, but capable of forming an alloy with each. **Hard soldering** or **brazing** is used chiefly for copper and brass, the fusible alloy employed being a brass rich in zinc; the ordinary **hard solder,** "spelter,"* for brass consisting of 1 part of copper and 1 of zinc, that for copper (and iron) having the composition of 2 of zinc to from 3 to 6 of copper. The melting point of the solder is of course chosen so as to fall below that of the metal to be soldered. This difference in melting point is indicated by the terms hard and soft spelter, the former being the less fusible. The flux used is borax, which is generally mixed with the solder, the latter being in the form of filings or wire. The mixture is made into a paste with water and applied to the joint, which is wired or pinned together so that it may not shift during soldering. The heating is effected by a coke fire or a gas blowpipe. Acetylene is occasionally used instead of coal gas. The action of borax as a flux is due to its power of dissolving metallic oxides, while leaving metals unattacked; cleaned metallic surfaces are thus presented to the action of the solder, a condition essential to the formation of alloys. **Silver solder** is another hard solder used for fine work in the same way and with the same flux as spelter. Hard silver solder contains 1 part of copper and 4 of silver, a softer variety containing 1 of copper and 2 of silver.

Soft solder is used for joining tin-plate and the more fusible metals and alloys—*e.g.*, zinc, lead, tin, and pewter. It is also largely used for brass and copper where strength of joint is not essential and the low fusing point of the solder is no detriment. Most varieties of soft solder are lead-tin alloys. **Fine solder,** the most fusible of common solders, contains 2 of tin to 1 of lead; **tinman's solder,** 1 of tin to 1 of lead; **common plumber's solder,** 1 of tin to 2 of lead; **coarse solder,** 1 of tin to 3 of lead; **pewterer's solder** consists of 2 of tin, 1 of lead, and 1 of bismuth, the object of the addition of the latter being to lower the fusion point below that of the pewter. Various fluxes are used, according to the nature of the metal to be soldered. Iron, which is less frequently soldered than the metals enumerated above, requires sal-ammoniac as a flux; for tin-plate, chloride of zinc solution or rosin is employed; for copper, any one of the three can be used; hydrochloric acid or zinc chloride is used for zinc; tallow for lead—*e.g.*, in "wiping" joints; and olive oil for pewter. Two classes of fluxes may he distinguished in this list. The first has a purely protective action, preventing the oxidation of the previously-cleaned metal surfaces; examples of this class are rosin, tallow,

* Spelter is used technically to mean (1) hard solder for brazing, and (2) cast zinc, as opposed to rolled or sheet zinc.

and olive oil. The second has a cleansing action, any oxide-film on the metal being fluxed and removed; sal-ammoniac, zinc chloride, and hydrochloric acid are cases in point. The use of these latter depends on the volatility and fusibility of most metallic chlorides. The choice of a flux depends mainly on the fusibility of the metal to be soldered, and on the readiness with which it oxidises. Thus tin (or tin plate), which does not easily oxidise and fuses readily, needs a fusible solder and a fusible flux which may be merely protective and have no cleansing action; such a flux is rosin. Copper is fairly non-oxidisable as compared with zinc or iron, and may be soldered with rosin, but zinc chloride is generally used. Zinc is a difficult metal to solder, as it is easily oxidisable and needs a cleansing flux. When hydrochloric acid is used, zinc chloride is formed *in situ*, but the zinc chloride can be also applied as such to the surface. In both cases zinc oxide is dissolved and a clean surface presented to the solder. The technical name for zinc chloride solution is "killed spirits of salt," it being made by "killing" spirits of salt (hydrochloric acid) by the addition of scrap zinc until saturation is reached. The soldering of iron and of copper is much facilitated by previous tinning, the process consisting in wetting the clean surface with pure tin before the soldering proper is performed.

A method of joining iron pipes where the joint will not need to be broken after it has been once made, consists in the use of a "rust-joint." The cement for this joint is made by mixing iron borings or filings (80 parts) with sal-ammoniac (1 part) and sulphur (2 parts), the whole being moistened with water and rammed into the joint. The joint is essentially iron rust, rapid rusting being induced by the minor ingredients.

Passing from mechanical causes of permanency or its opposite, **chemical agents** influencing the permanency of structural materials must be considered. The chemical agents which lead to the destruction of building materials are **water,** acting as a solvent and hydrating agent, **carbon dioxide,** and **sulphurous** and **sulphuric acids,** the last three acting simply as acid solvents in the presence of water. Nearly the only structural material suffering simple solution is plaster of Paris (calcium sulphate), including Keene's cement (*q.v.*, Vol. II.). On account of its solubility it is only used for work protected from the weather, or for temporary facing of hydraulic mortar exposed to the action of water, in order that the mortar may be protected while setting; the plaster is ultimately washed away, having fulfilled its function. The concrete itself, even when fully set, is not necessarily permanent when its structure is porous and water has free access to it, as hydraulic cements are by no means perfectly unaffected

by water. The presence in the water of salts with which the hydraulic cement is capable of reacting—*e.g.*, salts of magnesium—accelerates such change. Destruction may also be induced by the action of calcium sulphate in sea water brought into contact with hydraulic cement, inasmuch as this salt forms a definite compound with the calcium aluminate, $3CaO, Al_2O_3$, constituting an important part of the composition of the cement, and produces internal expansion or "blowing." As an hydrating agent, water will sometimes cause the disintegration of bricks which have been made from clay containing small lumps of chalk that have not been comminuted before the burning of the brick. The quicklime produced by the burning of these lumps expands in slaking, and splits off portions of the brick. When the chalk is thoroughly crushed and mixed it is harmless, as on burning, stable acid silicates of lime are formed, which do not expand by slaking on exposure to water. Carbon dioxide, sulphurous acid, and sulphuric acid have but little effect on dry structural materials, but are actively corrosive in the presence of water. It follows that all important parts of buildings should be protected from moisture, or well drained. Sandstone and brick, being acid materials, are not much attacked by these acid gases. Calcareous stones, on the other hand, being basic in character, are much corroded. The attack of calcareous stones is particularly severe in towns, where the air is laden not only with carbon dioxide, but also with sulphurous and sulphuric acids from the combustion of fuel, coal always containing sulphur (*v.i.*). The action of CO_2 on calcareous stones is due to the solubility of the earthy carbonates—*e.g.*, $CaCO_3$ and $MgCO_3$—in water containing CO_2. The activity of such strongly acid substances as SO_2 and SO_3 needs no special explanation. The more porous a stone, other things being equal, the more readily will it be corroded. Thus in the case of granite, which is almost perfectly impervious, corrosion is extremely slow, although the finely-divided stone is fairly easily attacked. Another corroding agent is atmospheric oxygen, when an oxidisable material such as pyrites is present in the stone. Pyrites (particularly the form known as marcasite) in stone or slate is oxidised by air and moisture to sulphates of iron, and causes disintegration and corrosion.

The **corrosion of metals,** which are completely impervious, necessarily proceeds wholly from without, and is more essentially due to oxidation than to the direct solvent action of acids, although the latter enhance the severity of the attack. The decay of iron, commonly known as **rusting,** is especially rapid and far-reaching, on account of the fact that the oxidation of iron is both attended by the evolution of much heat and is easily

initiated (*cf.* the oxidation of aluminium, *q.v.*), and also because the rust formed does not protect the rest of the iron, but rather increases its corrosion. It is probable that the simultaneous presence of water, oxygen, and an acid (generally carbonic acid) is necessary for the rusting of iron. In the absence of any one of these, but little rusting occurs. Moreover, the presence of an alkali, or even an alkaline carbonate,* prevents the rusting of iron. The rusting of iron may be viewed as taking place in two stages, according to the equations—

$$(1)\ Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$(2)\ 2FeCO_3 + 3H_2O + O = Fe_2(OH)_6 + 2CO_2$$

Taking this view of the change, it is apparent that a small amount of CO_2 may be instrumental in rusting an indefinitely large amount of iron. The elimination of hydrogen in the first stage of the reaction causes the removal of carbon (as hydrocarbons) from iron containing that element.† It has been shown that **rust** is not pure hydrated ferric oxide, but contains hydrated ferrous oxide, the two being at least partially present as hydrated ferroso-ferric oxide, which accounts for the fact that common rust is attracted by a magnet. This intermediate state of oxidation may arise from the action of hydrated ferric oxide on iron, yielding hydrated ferrous oxide. This latter may in turn oxidise and act upon the remaining iron, the hydrated ferrous oxide serving in fact as a carrier of oxygen from the air to the iron. The rate of rusting of grey cast iron is generally slower than that of wrought iron or ingot iron. These two forms of the metal corrode the more rapidly with rising content of carbon, a generalisation which extends to cast steel and white cast iron containing much combined carbon.

Rust will generally contain its constituents in proportions exemplified below :—

	Per cent.
Moisture,	11·77
Siliceous matter,	3·33
Fe_2O_3,	66·82
FeO,	3·99
CaO,	0·76
MgO,	Trace.
CuO,	Trace.
Combined H_2O and loss,	13·33

* In certain cases, however, it is found that ammonium carbonate will induce rusting.

† Dunstan and others have recently put forward the view that the presence of oxygen and liquid water only is necessary for the rusting of iron; that carbon dioxide plays little, if any, role; and that hydrogen peroxide is probably always formed as an intermediate product.

Rusting is increased by **galvanic action** set up by contact of the iron with a metal electro-negative to it—*e.g.*, copper or tin. Thus, tin plate rusts more rapidly than unprotected plate at any spot from which the tin has been removed, the surrounding tin forming a galvanic couple with the exposed iron. The corrosion of iron railings, set at their foot in lead, which takes place very locally just above the point of contact of the two metals, is due largely to galvanic action. The same applies to iron protected by a film of copper rolled on or electrolytically deposited; the protection is satisfactory only as long as the coating is perfect. With zinced iron, on the other hand, slight imperfection of the coating are of less importance, as the zinc is electro-positive to iron and is the attacked metal of the couple, the exposed iron being protected at the expense of the zinc. This protection, though useful when the zinced iron is uniformly wetted, is not necessarily effective when the metal is only sprinkled with moisture, as a given spot of water may be exclusively in contact with the iron, and thus no couple may be formed. Zinced iron is not very resistant to salt water and sea air, the zinc being rapidly stripped by the action of chlorides, and the iron exposed. Two pieces of iron of different kinds may also form a galvanic couple, and increase the rate of rusting. Iron of all sorts is far from perfectly homogeneous, and this want of uniformity may lead to local rusting without contact with any other metal. Thus, wrought iron often contains slag unevenly distributed, and the loose porous places caused by the presence of the slag are good starting points for "pitting." Ingot iron may contain manganese disposed irregularly, and pitting may result from this circumstance.

This kind of corrosion is illustrated by the attack of propeller shafts at the point where they project from their brass sheathing; this has been found so serious as to necessitate special methods of protection. (The corrosion of iron is also discussed in Chap. iii., p. 142.)

Copper is less easily oxidised than iron. When exposed, however, to moist air, it is attacked, with the formation of basic carbonate of copper, a bluish-green film being formed. On account of the readiness with which copper is attacked by cupric salts—the cuprous salts formed serving as oxygen carriers—progressive corrosion is to be expected. The presence of an acid gas enhances the corrosion and particularly increases its progressive character. If the acid gas be HCl, or if the copper be exposed to a solution of salt (in the presence of air), the corrosion is caused by the formation of an oxychloride instead of a basic carbonate. Although attacked by sea water, copper is less

rapidly corroded by this agent than is iron, and on this account has been used for sheathing ships. The copper salts formed, moreover, constitute by their poisonous action a certain protection against fouling by marine growths. Copper for vessels for containing or conveying articles of food or drink are thickly **tinned** on the inside, the melted tin being wiped upon the cleaned surface of the copper in the presence of a flux, as in soldering. Where strength and resistance to accidental overheating are not essential pure tin may be substituted for tinned copper with advantage. Silvered copper and pure silver are also used in special cases—*e.g.*, in the worms of acetic acid stills. The behaviour of most copper alloys—*e.g.*, brass—in respect of corrosion is similar to that of copper, but copper-tin alloys, as, for instance, bronze and gun-metal, are less easily attacked than copper itself. In the case of Muntz metal, the zinc is very slowly dissolved out by electrolytic action, leaving a skeleton of copper behind. Statuary and ornamental bronze gradually acquires by exposure a protective film, ranging in colour from green to nearly black, which is termed a "patina," and improves the appearance of the metal. An artificial patina may be produced by slightly corroding the surface of copper and its alloys by such saline solutions as ammonium chloride in conjunction with copper salts. Treatment of this kind comes under the general head of **metal colouring**; for details, special manuals must be consulted.

Copper aluminium alloys (aluminium bronzes) are remarkable for their resistance to corrosion, and on this account are used for ships' fittings, propeller blades, and filter press plates, where their cost is not excessive. The fact that aluminium alloys with copper with the occurrence of an exothermic reaction, doubtless contributes to the stability of the alloy.

Zinc oxidises superficially in moist air, but the coating of zinc oxide or basic carbonate produced affords sufficient protection for the underlying metal. When acid gases are present in the air, or when the metal is in contact with solutions of chlorides, the film dissolves and corrosion proceeds. Contact with an electro-negative metal or the solution of a salt of one—*e.g.*, copper—is particularly fatal to zinc, as a couple is formed, and then corrosion proceeds at a rate to be expected from the oxidisable character of zinc. Pure zinc is very difficult of attack; commercial zinc, containing lead, is more readily corroded, as it has within it the elements of a couple. Zinc, when used in the form of the coating on zinced iron, for pipes and cisterns, resists the action of calcareous, slightly alkaline waters well, a coating of basic carbonate protecting the metal. Soft waters containing traces of organic acids and nitrates (which suffer reduction to

ammonia), however, attack zinc appreciably, and zinced pipes are unsuited for their conveyance, the more so as any exposed iron forms a couple with the zinc and increases its rate of corrosion. Zinc salts being somewhat toxic, their presence in drinking water is objectionable. It has been found that zinc is sometimes attacked when in contact with cement, mortar, or brick. In the case of the first two, corrosion appears to be due to the *alkaline* substances present, zinc being soluble in *alkalies*; the latter acts by the presence in it of soluble salts, notably chlorides.

Lead oxidises with great ease when exposed to air, but the oxidation is exceedingly superficial, and the film is protective. The case is quite otherwise when carbonic acid is abundant and an organic acid present, a crust of basic lead carbonate being formed by an action similar to that taking place in the manufacture of white lead by the Dutch process (*q.v.*, Vol. II.). Complete conversion of the original lead into crude white lead may thus occur. On account of the cumulative toxic effect of lead, its presence in drinking water is very objectionable. Soft waters, especially if containing traces of organic acid—*e.g.*, moorland peat waters—dissolve the lead oxide first formed, and leave the metal exposed for further attack. Slightly alkaline calcareous waters have no corrosive effect. The solvent effect is increased or decreased by pressure (such as obtains in water mains), according to the character of the water; direct experiment is, therefore, necessary to decide the behaviour of any given sample. It will be seen that it is hardly possible to lay down rules for the guidance of the water engineer, who is thus ultimately dependent, as in most similar cases, on the aid of the chemist.

The character of the corrosion of aluminium is dealt with under the description of the metal itself (see *Metallurgy*). It may be said here that aluminium has been found, when pure, to resist the corrosion of most articles of food and drink. The feebleness of the toxic action of aluminium salts makes the small quantity of the metal taken into solution of no practical importance.

Nickel is more difficultly oxidisable than any of the foregoing metals. It tarnishes in moist air, but the attack is purely superficial. It resists the joint action of salt water and air better than do most common metals. Weak acids attack it with moderate ease, but it is used for cooking vessels to some extent. Its alloy with iron (75 per cent. Fe, 25 per cent. Ni), though more readily corroded than nickel, is still very resistant, and may replace brass, copper, and plated goods for many minor purposes, the more so as it can be stamped and spun. As will

be seen from the following table, due to Prof. Howe, nickel steel (*containing about 3 per cent. of nickel) is more resistant than* either wrought iron or mild steel. The specimens were exposed for one year, and the corrosion of the wrought iron is in each case taken as 100 :—

Material.	Sea Water.	Fresh Water.	Weather.	Average.
Wrought iron, . . .	100	100	100	100
Soft steel, . . .	114	94	103	103
Nickel steel (3 per cent.). .	83	80	67	77
Nickel iron alloy (26 per cent.)	32	32	30	31

Timber is subject to deterioration by reason of the mechanical effects of ordinary wear and tear, conditions of climate, and from the action of insects, such as ants and worms. More important, however, is the decay of wood due to the growth of bacteria and fungi. These bring about changes in the wood substance itself by producing certain complex chemical substances known as ferments, which decompose the cellulose and lignin forming the wood cells. The fungoid growth depends upon the presence of moisture, warmth, and air, and, moreover, is much more rapid in sapwood, the cells of which contain fermentable substances, than in heartwood.

METHODS FOR THE PRESERVATION OF STRUCTURAL MATERIALS.—The preservation of stone and brick may be effected by making them non-porous, and for this, various means may be used. Glazing is occasionally practised for bricks and tiles used for indoor work ; the objections to it for outdoor work have been stated under tiles (p. 30). By the application of a fatty or oily varnish which will soak into the stone (or brick) the surface may be rendered non-porous, but since most materials of this nature are far less durable than the stone itself, repetition of the process at intervals of a few years is necessary. Varnishes of this kind include drying oils, paraffin wax applied hot or in solution in coal-tar naphtha, and soft soap followed by an aluminium salt in order to precipitate the aluminium salts of the fatty acids of the soap in the pores of the stone. These materials, however, deteriorate the appearance of the stone. A preservative of a different order is silicate of soda applied to calcareous stones (calcium silicate and sodium carbonate being produced). The successive treatment of sandstones with silicate of soda and calcium or barium chloride is also practised (calcium

or barium silicate and sodium chloride being formed); in this case the stone is treated with silicate of soda, allowed to dry, and then saturated with the alkaline earth chloride. A similar preservative material is obtained by the successive use of hydrofluosilicic acid and baryta, insoluble barium fluosilicate being deposited. The last-mentioned process has the advantage that no soluble salt is formed in the stone, and thus efflorescence is avoided. The only process of protecting stone which is largely used is the application of ordinary paint. With regard to the use of any preservative coating which renders the stone or brick impervious, it may be said that ordinary structures of porous untreated material, though absorbing moisture readily, allow its egress to take place equally readily, and offer no hindrance to transfusion of air through their walls. A building with impervious walls, although excluding damp from without, includes internal damp, and allows no ventilation other than through definite openings (windows, &c.) to take place.

Iron is the chief metal for the protection of which special preservative coatings are in use. Zincing for effecting this purpose has already been described. As it cannot be renewed *in situ* it is not used for permanent non-portable structures. A method of protecting, and at the same time ornamenting, iron, largely used for sign-boards and cooking vessels, consists in **enamelling** it.* The details of the process are for the most part kept as a trade secret, but its principle is very simple. A preliminary glaze is given to the iron by fusing an appropriate frit (see *Pottery*, Vol. II.) on it in a muffle, and the metal is then coated with a second layer of more fusible glaze by a further similar treatment. *The object of the first glaze is to provide a film intermediate in* respect of its coefficient of expansion between the iron and the exterior glaze.

Moreover, the stannic oxide which is always present in the second layer would be reduced by the carbon contained in the iron at the temperature of the muffle, and cause the development of blisters. The first layer or "ground enamel" is essentially an easily fusible substance containing definite amounts of borax with cobalt or nickel oxide and a little limonite (hydrated ferric oxide), the proportions of which determine its coefficient of expansion. In order to produce a sufficiently fusible glaze, lead oxide was formerly an almost invariable constituent of both glazes, and is still used largely by makers of cheap enamel ware. From a hygienic standpoint this is objectionable in the case of glazed cooking vessels, besides being a source of danger to the workmen

* The processes will be found fully described in *Enamelling on Iron and Steel*, by Julius Grünwald, London, 1910.

employed. Moreover, an enamel containing lead is found to be somewhat unstable when exposed to the weather. In recent years an important advance has been made in the gradual but successful supplanting of lead glazes by harmless, inexpensive, and more durable enamels, especially in countries such as Germany and Austria-Hungary, in which the use of lead (and antimony) compounds is forbidden. Enamel is merely a coating of glass containing an ingredient such as stannic oxide, bone ash, or titanic acid (TiO_2) to render it opaque. Various metallic oxides may be added to impart colour, but white is the most common variety of enamel used. The ingredients of the enamel, having been ground and mixed, are completely vitrefied in a reverberatory furnace, and then granulated in water. The enamel is then ground with water, with the addition of stannic oxide for developing a good white colour in the enamel, and clay which has the capacity of holding the enamel in a state of suspension and prevents it from "settling." In some cases certain other ingredients are added during the grinding process, such as calcined magnesia and ammonium carbonate, which serve as *vehicles to stiffen the enamel, and various coloured oxides.* The nature of these enamels may be judged from the following formulæ:—

Ground Enamel.		White Enamel.		Addition on Grinding.
Borax ($Na_2B_4O_7 . 10H_2O$) .	= 39·6	Borax . .	= 40·3	
Felspar ($6SiO_2 . Al_2O_3 . K_2O$)	= 30·7	Felspar .	= 39·0	
Quartz (SiO_2) . . .	= 17·2	Soda . .	= 2·6	Stannic oxide, 7 %
Soda (*Na_2CO_3*) . . .	= 4·6	*Cryolite* .	= 13·0	Clay, . . 7 %
Fluorspar (CaF_2) . .	= 4·0	Saltpetre .	= 2·0	Magnesia, . 0·3 %
Saltpetre ($NaNO_3$) . .	= 3·0	Clay . .	= 1·6	
Cobalt oxide (Co_2O_3) . .	= 0·2	Stannic oxide	= 1·3	
Limonite ($2Fe_2O_3 . 3H_2O$) .	= 0·7	*Magnesia* .	= 0·1	
		Fluorspar .	= 0·1	
	100·0		100·0	

The iron to be enamelled is prepared by annealing, pickling, scouring, and washing. It is then coated with the enamel, carefully dried in ovens, and fired in a muffle furnace. For the first layer a temperature of 950°-1,000° C. is used, while for subsequent layers a somewhat lower temperature (800°-850° C.) is usual. The time of firing is abont four minutes. The common method of decorating enamel ware is by means of transfers *printed with ink made with fusible oxides. The transfer is*

attached to the enamel surface, and the ornamentation fixed by firing.

Another method, in which the protective coating is made from the iron itself, is that known as the **Bower-Barff process.** In this the goods are heated in a muffle to about 538° C. = 1,000° F., and steam, superheated to about the same temperature, is admitted into the muffle. The iron decomposes the steam, becoming coated with black ferroso-ferric oxide. The depth of this coating is regulated by the length of the process, and may be as much as $\frac{1}{16}$ in. The protection is good as long as the coating is intact; it is stated that when the ferroso-ferric oxide is chipped off, the rusting of the iron exposed is more rapid than that of untreated iron. A method adapted for imparting a similar coating to articles of moderate size consists in immersion of the polished goods in a bath of melted nitre containing a little manganese oxide, and maintained at a temperature of 650° F. = 343° C. After cooling, the adhering nitre is dissolved off and the article plunged into a sperm oil bath. In another process for superficially oxidising iron to form a protective coating, the article is immersed in water and made the anode of an electric circuit, a film of ferroso-ferric oxide being formed. The **Coslet process** is said to consist in immersing the iron in a hot phosphorised solution containing an iron compound. The surface, it is claimed, is converted into a ferroso-ferric phosphate, which is to some extent resistant to corrosion.

None of the foregoing processes is adapted for the protection of structural materials when in place. For the preservation of structures already erected **paint** alone is available. The paint most generally in use for iron structures (bridges) is a **red oxide paint** consisting essentially of Fe_2O_3 (see *Paints*, Vol. II.). The quality of the ferric oxide used for making this paint is of much moment, some being perfectly unsuitable from the presence in it of basic ferric sulphate, which tends to corrode the iron to which the paint is applied. **Red lead paint** appears to be the best for iron work. It should be free from metallic lead (often present), which is liable to cause galvanic corrosion. The surface of the metal should be scraped scrupulously clean and free from scale, and a coat of boiled linseed oil applied before the painting proper is performed. A method of protecting iron water pipes, which is effective when carefully carried out, consists in the application of **Angus Smith's composition.** The pipes are cleaned from scale, heated to 700° F. = 371° C., and dipped into a mixture of coal tar, pitch, and a little linseed oil (about 5 per cent.), and sometimes rosin, which is heated to about 300° F. = 149° C. The pipes are dipped vertically,

allowed to remain for some minutes in the bath, and then permitted to cool and drain in a vertical position. Glass-lined iron pipes are also made for conveying corrosive liquids and gases. They are prepared by cementing glass tubes into iron pipes of slightly larger diameter, bends and T pieces being blown on to the main pipe precisely as in ordinary chemical glass blowing.

Anti-fouling compositions are largely used for protecting the bottoms of steel ships from the growth of marine animals and plants upon them. The problem of preventing the growth of marine life on the hull of a ship has been attacked from two points of view—(1) compositions have been applied which have for their object the prevention of the adhesion of barnacles and seaweed by affording an unstable foothold for these organisms. Thus a paint made of zinc oxide (white zinc) and tallow fulfils this condition. It is applied as a second coat after a preliminary coat of paint—*e.g.*, red or white lead. This material causes the growths to slip off when they have attained a certain age. For vessels of high speed such a paint is useless, as it is rapidly washed off: the second method has, therefore, to be employed. (2) Compositions containing a substance inimical to marine life are also in use. An example is furnished by a preparation containing mercuric oxide suspended in a shellac varnish containing crude turpentine or Stockholm tar. The varnish is soft enough to be slowly eroded, and thus to expose the mercuric oxide, which serves to poison any organism finding a temporary foothold. The use of a mixture of finely-divided zinc and mercuric oxide, made into a soft varnish, has also been suggested. It is claimed that this composition is effective by reason of the fact that when the mercuric oxide dissolves, mercury is deposited on the zinc, and when the zinc dissolves mercury is left in the varnish, and dissolves more slowly than mercuric oxide. A method for protecting iron, more particularly used for boilers (*v.i.*), consists in attaching to the metal, plates of a substance electropositive thereto—*e.g.*, zinc, the process being equivalent to local galvanising. It is obvious that this process is only effective when the whole of the surface to be protected is immersed as in the case of a boiler; the attack is then confined to the electropositive metal—*e.g.*, the zinc. The same system has been applied to the protection of copper dye baths, the corrosion of which is objectionable on account of the effect of the traces of copper upon the colour of the contents of the vat.

Ornamental iron goods are often plated electrolytically with nickel. As nickel is electronegative to iron the coating is only effective as long as it is intact; when injured it enhances

corrosion instead of preventing it. The same is true of plating with copper on iron.

No other metal is at once so freely exposed and so corrodible as iron, and special methods of protection are, therefore, rarely used for copper and its alloys, or for lead, zinc, etc. When plating with copper, nickel, silver, or gold is adopted, it is rather for ornament than for protection.

The **preservation of timber** depends largely on the protection of the wood from moisture which favours the growth of the low organisms concerned in its destruction. To this end the wood should be well ventilated, and, it is said, kept from contact with mortar. Timber must not be used before the sap is dried out of it, since this contains easily fermentable substances. The sap can be replaced by a preservative—*e.g.*, coal-tar creosote, wood creosote, zinc chloride, mercuric chloride, or copper sulphate. Such treatment becomes necessary when the wood is to be used in wet situations or under water. The most direct method for the preservation of wood consists in applying a pump to the butt end of the freshly-felled tree and injecting zinc chloride solution of specific gravity 1·01, the sap being driven to the smaller end of the tree and gradually extruded. (The same process may be adapted so as to colour timber; a tree may be coloured brown by the injection of weak sulphuric acid, or mahogany red by nitric acid.) A larger proportion of zinc chloride remains in the butt end than in the distal end, and thus the preservative effect is somewhat irregular; the chief merit of the process consists in the ease with which timber can be treated at the spot where it has grown, without transport being requisite. Zinc chloride is also used in the same manner as creosote, the application of which is described below; the solution of zinc chloride thus employed is known commercially as **Burnett's fluid.** Mercuric chloride may be substituted for zinc chloride, its application being known as **kyanising.** Copper sulphate, forced into the wood by leading a solution of the salt from an elevated reservoir by means of a pipe which is inserted into the log, is also used, the method being known as **Boucherie's process.** **Creosoting** is most largely used for preserving timber, especially railway sleepers. Coal-tar creosote (see *Coal-tar*, Vol. II.) is generally used in this country, the grade required being a dark mobile oily liquid of specific gravity 1·035 to 1·055 and containing about 5 to 15 per cent. of tar acids (phenol and its homologues), and about 40 per cent. of naphthalene. There is no agreement as to which compounds are to be considered as specifically important in increasing the preservative action of creosote. The more volatile portions should be reduced as far as possible

consistent with obtaining an oil sufficiently fluid at all working temperatures to obtain a thorough and equal penetration throughout the wood cells. Its efficiency largely arises from the fact that it serves to fill the pores of the wood with an insoluble inert oil which prevents the entrance of water and the growth of organisms. Creosoting is conducted by introducing the well-seasoned timber into steel cylinders about 36 feet long and 6 to 7 feet in diameter. The air is then exhausted from the cylinder until a pressure of about 2 lbs. per square inch remains. The creosote oil is heated to 50° C. = 122° F., run into the cylinder, and forced into the wood by a pressure of 120 to 150 lbs. per square inch. The pressure is maintained for several hours, the timber, if pine, absorbing about 12 lbs. of oil per cubic foot of wood. Large pieces of wood often show a core free from oil, as uniform impregnation is difficult. In America, where but little coal is carbonised and wood is cheap, wood creosote has been successfully used for the preservation of piles exposed to the attack of the teredo. The character of the oil used may be gathered from the products said to be yielded on distillation, as shown by the following analysis:—

	Per cent.
Water,	2·79
Neutral oil,	13·16
Crude creosote (wood-tar acids),	17·00
Heavy oil,	26·55
Paraffin wax,	25·97
Coke,	5·78
Uncondensed.	8·75
	100·00

The foregoing methods are analogous in principle to the impregnation of stone with preservative solutions (p. 50). Other methods of preserving wood consist in applying a superficial protective coating. It is important that this should not be done until the wood is well seasoned, since if moisture be prevented from escaping the wood will rot. ("Dry rot" is due to the action of a fungus.) Coatings of this kind include paints and tar (coal or wood, the latter being more effective). Another method adopted for wood—which is comparable in principle with the Bower-Barff process, inasmuch as the material to be preserved itself furnishes the preservative coating—consists in superficial charring. This is chiefly used for preserving posts and stakes to be inserted in moist soil.

Wood is rendered **fire-proof** by filling its pores with a mineral substance, the process being carried out in much the same way

as creosoting (*v.s.*). A large number of different solutions are used for this purpose. Most of them contain an alkali silicate from which silica is often precipitated by treatment with a second liquid—*e.g.*, ammonium chloride solution. Uranium and tungsten salts are also used for fire-proofing. It should be said that in most cases the treatment only prevents the wood from breaking into flame when heated to its ignition point, but does not prevent it from smouldering away quietly. Many of the chemicals used for fire-proofing are hygroscopic, and consequently hasten the rotting of wood impregnated with them.

CHAPTER II.

THE CHEMISTRY OF THE SOURCES OF ENERGY.

EVERY form of energy on this planet can be traced to one of three sources. These are (1) the heat of the sun, (2) the rotation of the earth, (3) the internal heat of the earth.

The first is at present by far the most important. The kinetic energy pouring from the sun as heat and light can be with difficulty industrially utilised directly, but as the ultimate source of waterpower is of great and increasing importance. The energy which has been derived from the sun and become potential in the form of fuel is readily utilised, and has been hitherto the only practicable source of energy for industrial purposes. The second is of minor importance, being represented only by the energy manifested by the rise and fall of the tide: no successful attempt has hitherto been made for its utilisation. That the third undoubtedly exists as a source of energy is proved by the occurrence of volcanic phenomena; its utilisation belongs to the future.

Potential energy in the form of stored heat from the sun will, therefore, be chiefly considered in the ensuing pages; the other and minor sources of energy will be dealt with subsequently.

Fuel may be defined as any substance capable of exothermic oxidation with sufficient rapidity to leave an available balance of energy after the leakages of energy surrounding the point of combustion (*e.g.*, radiation, convection, and conduction) have been supplied. It is obvious that *cæteris paribus* the available balance will be larger the more concentrated the fuel—*i.e.*, the smaller the quantity of matter it contains which, on the one hand, is incapable of contributing to its exothermic oxidation, and, on the other, augments the loss by leakage. From this it follows that for two equal weights of the same oxidisable material, the fuel which contains, in addition to the oxidisable material, the smaller quantity of inert matter will tend to give a higher thermal efficiency; for the larger weight and bulk of the more impure fuel will lead to larger leakage by conduction, convection, and radiation. By far the greater part of the fuels industrially

Class of Coal.	C.	H.	O.	Coke.	Character of Coke.	Sp. gr. of Coal.	Calorific Value.*
	Per cent.	Per cent.	Per cent.	Per cent.			Calories.
Dry coals burning with a long flame,	75-80	5·5-4·5	19·5-15	50-60	Pulverulent or slightly sintered,	1·25	8,000-8,500
Caking coals with long flame (gas coals),	80-85	5·8-5	14·2-10	60-68	Intumesced; semi-fused,	1·28-1·30	8,500-8,800
Caking coals proper, forge coal, coking coal,	84-89	5·5-5	11-5·5	68-74	Coherent and fairly dense,	1·30	8,800-9,300
Caking coals with short flame,	88-91	5·5-4·5	6·5-5·5	74-82	Coherent and very dense,	1·30-1·35	9,300-9,600
Anthracitic or lean coals burning with short flame,	90-93	4·5-4	5·5-3	82-90	Pulverulent or slightly sintered,	1·33-1·40	9,000-9,500

* By this is meant the number of kilos. of water which the combustion of 1 kilo. of coal will raise from 0° to 1° C.

used consists of carbon; elements whose combustion is also used in minor degree are hydrogen (chiefly in union with carbon, but also in the free state), sulphur, as native sulphur (Vol. II.), and as pyrites (*cf.* concentration of vitriol in the Glover tower, Vol. II.), and silicon, phosphorus, and manganese in the Bessemer converter (see *Ingot Iron* under *Metallurgy*). See Table, p. 59, for the chief kinds of fuel.

A. **SOLID FUEL.**—COAL.—Many varieties of carbonaceous matter, known generically as coal, are used as fuel. Of these **coals,** considered as distinct from **brown coals** and **lignites,** the foregoing groups may be distinguished, according to Gruner's *classification which is based upon the technical use of the* coals.

The different qualities which are found have no clear line of demarcation between them, so that their classification, as will be seen from the table, is necessarily somewhat arbitrary.

The figures tabulated above are for ideal coals, free from sulphur, ash, water, and nitrogen, which are constituents of all actual coals, and range from 1 to 30 per cent. for ash, 0·5 to 2 per cent. for sulphur, 0·1 to 9 per cent. for water, and 0·2 to 2 per cent. for nitrogen. Many coals also contain a small quantity of arsenic, whilst phosphorus is occasionally present. A good coal will not contain much more than 5 per cent. of ash, 1 per cent. of sulphur, 2 per cent. of water, and 1 per cent. of nitrogen. Besides the above ordinary varieties of coal, two kinds need special mention. True **anthracite** is distinguished from anthracitic coals by *containing a still higher percentage of carbon and a still* smaller percentage of oxygen and hydrogen. In appearance it is deep black, but it does not stain the fingers in the manner characteristic of bituminous coal. Its fracture is conchoidal, and its specific gravity may be as high as 1·7. It burns with a very short flame, and shows no tendency to sinter in the fire, but often decrepitates in the act of burning. Seeing that the amount of flame with which a given coal burns increases with the content of hydrogen, and that the larger the flame produced the more easily a coal is kindled, it follows that anthracite is nearly flameless and is also difficult to ignite, a circumstance militating against its domestic use. The second kind of coal needing special description is **cannel,** which is distinguished by a large content of hydrogen over and above that corresponding with the oxygen in the ratio $H_2 : O$ (*v.i.*), and, therefore, available for gas production (see *Destructive distillation,* Vol. II.). Analyses of these two extremes of the whole series of coals are as follows:—

	C.	H.	O.	N.	S.	Ash.	Water.
	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Swansea anthracite,	90·58	3·60	3·81	0·29	...	1·72	...
Boghead cannel,	65 3	9·1	5·4	0·7	0·1	18·6	0·5

The total amount of heat that can be produced by the combustion of a given weight of coal can be ascertained either by calculation from the composition of the coal or by direct experiment. On account of incomplete knowledge of the conditions in which the constituents of coal exist, the calculated **calorific value** is only approximate to the truth, being generally considerably below the experimental value. It is customary to determine the percentage of C, H, N, and S in the coal by analysis, to take O by difference, and to calculate the calorific value on the basis of the facts that the complete combustion of 1 kilo. of carbon evolves 8,080 Cal., while 1 kilo. of hydrogen gives 34,400 Cal., and that the heat evolved by the combustion of the sulphur is so small as to be usually negligible. Further, it is assumed that the oxygen present is combined with hydrogen in the same proportion as it is in water, and that the amount of hydrogen thus combined is not available for the production of heat when the coal is burned. Thus the number of calories evolved by the combustion of 1 kilo. of coal will be given by the formula $8,080 \text{ C.} + 34,400 \left(\text{H} - \frac{\text{O}}{8}\right)$, where C, H, and O represent the respective parts by weight of these elements in one kilo. of coal.

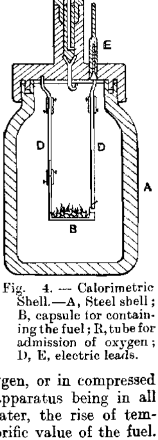


Fig. 4. — Calorimetric Shell.—A, Steel shell; B, capsule for containing the fuel; R, tube for admission of oxygen; D, E, electric leads.

The direct determination of the calorific value of the fuel may be made by burning a known weight with a mixture of oxygen-yielding substances, or in a stream of oxygen, or in compressed oxygen in a confined space, the whole apparatus being in all cases immersed in a known weight of water, the rise of temperature of which is a measure of the calorific value of the fuel. For practical reasons the last plan is the best. It can be carried out in the apparatus shown in the figure (Fig. 4). This consists

of a steel shell, A, lined with white enamel, platinum, or gold, and having a capacity of 650 c.c.; a cover provided with a lead washer, screws on to the body of the shell. A weighed quantity of fuel—*e.g.*, 1 gramme—is placed in a capsule, B, and oxygen is admitted from a cylinder of the compressed gas through the tube, R, made of nickel-iron (pp. 28 and 50), and serving as a screw-valve, until the pressure, as shown by a gauge, is 20 to 25 atmospheres. The valve is then closed, the shell immersed in the calorimeter, and the fuel ignited by means of an electric current traversing a fine iron wire spiral which passes through the fuel and is attached to the two platinum rods, D, which support the capsule. The current is conveyed through the insulated conductor, E, which passes through the lid, the other electrode being attached to the shell. The rise of the temperature of the water in the calorimeter during the experiment is noted by means of a delicate thermometer.

The utility of a coal depends not only on its calorific value, but on its character in respect of its content of bituminous gas-yielding matter, and of the nature of the coke formed by its partial combustion or destructive distillation. The progress of combustion of a coal in an ordinary furnace involves the destructive distillation of a portion of it, whereby gases are evolved which determine the nature of the flame produced. Judgment of the properties of a given coal in this respect is based on the figures yielded by its proximate analysis, which is effected by heating a weighed quantity of the coal in a covered crucible under standard conditions, and estimating the fixed carbonaceous matter, plus the ash, as coke. (The yield of coke by different kinds of coal has been given in the tabular classification of coals —p. 59). The ash is also determined, and the difference between this and the coke constitutes the fixed carbonaceous matter.

It may be broadly stated that coal is used for steam-raising, household fires, gas-making, and metallurgical operations. For the first of these uses a hard "steam coal" of a semi-anthracitic kind is most esteemed, as it has a high calorific value, produces little ash and clinker, and does not smoke. For household fires a more freely burning and more bituminous coal is requisite; one which cakes is economical, as the fire can be readily damped down. For gas-making, bituminous coals with a fair content of hydrogen are requisite (see *Destructive distillation*, Vol. II.); the quality of the coke formed is of minor importance. For metallurgical use much coal is coked (see *Destructive distillation*), and for this purpose caking bituminous coal is generally preferred. Both flaming and anthracitic coals are used, according to the nature of the work to be done. With regard to the common impurities

of coal, it may be said that ash should be present to a minimum extent, as the grate is blocked and impeded by the dust and clinker produced by a fuel rich in ash, which, moreover, causes a small waste of heat in being raised to a high temperature during combustion and being removed from the grate before it has given up this heat. Sulphur also is objectionable on account of the contamination of the surrounding air by chimney gases containing the sulphur of the coal in the form of sulphurous and sulphuric acids. Water is objectionable, as it has to be evaporated, involving the useless expenditure of heat. Nitrogen is not of much detriment in coal, as the waste of heat occasioned by raising its temperature is not serious (as it is always present in only small proportion). In gas coals it has a certain commercial value, in that a portion of it is recovered as ammonia (see *Destructive distillation*). Attempts have been made to recover the nitrogen in a useful form from the coal burned in ordinary furnaces, but success has only been achieved hitherto in the case of blast furnaces and certain forms of producers. Coal suffers diminution of its calorific value by exposure to air and moisture (*weathering*). This alteration is due to oxidation, and is accompanied by a gain of weight, which in extreme cases may amount to as much as 4 per cent. Pyrites, which is constantly naturally present in coal, also suffers oxidation to some extent, but is not as fruitful a cause of spontaneous ignition as has been supposed, this phenomenon being due to the oxidation of the less stable carbonaceous constituents of the coal. Such spontaneous ignition takes place more readily when the coal is crushed and exposed to a warm atmosphere, as in the bunkers of a steamship. The quality of coal may be improved by systematic washing; the coal is thus graduated in size, and, by taking advantage of the difference of specific gravity between coal on the one hand and shale and pyrites on the other, a diminution of ash content is also effected, the sulphur (due to the pyrites) being correspondingly reduced in amount. The general mechanical arrangements of apparatus for **coal-washing** are identical in principle with those used for sizing and concentrating ores (see *Gold*).

COKE is carbonised coal containing the whole of the ash of the original coal and the greater part of the carbon, but comparatively small amounts of H, O, S, and N. Two classes of coke may be broadly distinguished. The first is that which is manufactured by processes of which the coke is the main product, and the other substances formed by the destructive distillation of the coal are the bye-products. It is made in coke ovens for metallurgical consumption; its manufacture is treated of in the section dealing with destructive distillation (*q.v.*, Vol. II.). The second class of

coke is that obtained as a bye-product in carbonising coal for gas-making, where the main products are gas and tar. The advantages of coke over ordinary coal, as distinguished from anthracite, which is relatively expensive, are that it contains a larger percentage of carbon, and, therefore, takes up less space in the furnace; that it does not cake, thus offering less resistance to the blast; that it yields a higher thermal efficiency, as it does not give off large quantities of hot and combustible gases; and that it contains less sulphur than the coal from which it is made. "Oven coke" is denser and of greater mechanical strength than "gas coke," and is, therefore, better fitted to carry the burden of the blast furnace (see *Iron*). Moreover, oven coke resists the oxidising action of hot CO_2 better than does a coke of looser structure, and thus suffers less waste in the upper part of the blast furnace. These qualities warrant the metallurgical use of oven coke in spite of its greater cost; the cost has been largely diminished of late years by the collection of bye-products (see *Destructive distillation*, Vol. II.). Good dry oven coke contains about 90 per cent. C, 1 to 2 per cent. H, 1 to 2 per cent. O, 1 per cent. S, 1 per cent. N, and 5 per cent. of ash; it has a calorific value of about 8,000 Cal.; it generally contains 2 to 3 per cent. of moisture, but this amount is exceeded when it has been carelessly quenched after coking. Seeing that the yield of coke is about 66 per cent. of the weight of the coal carbonised, the percentage of ash will be increased in inverse ratio. Thus a coal containing 5 per cent. of ash will yield a coke with 7·5 per cent. For blast furnace use, the amount of ash should not exceed 5 per cent., and for metallurgical use generally the percentage of sulphur should be as low as possible—1 per cent. or under. Not only is ash in coke objectionable as being valueless, but it is actively injurious in some instances on account of its chemical nature. The ash of most coals, and, therefore, that of the corresponding cokes, consists largely of silica, alumina, and ferric oxide—all substances capable of acting as acid oxides when brought into contact with powerful bases (*e.g.*, lime) at high temperatures; consequently, wherever the manufacture of a substance such as quicklime or hydraulic cement involves the admixture of the fuel with the raw material to be burned, there is ample opportunity for the ash of the former to combine with the latter, to its detriment (see *Lime* and *Cement*, Vol. II.). As much gas coke contains a large amount (up to 30 per cent.) of ash, its chief manufacturing uses—in cement-making and in gas producers—is attended by considerable drawbacks; its cheapness is its main recommendation. Among the smaller uses to which coke is put are the heating of metals and tools, and of articles to

be brazed, where the comparatively dirty flame of coal would be unsuitable. As coke still contains some sulphur, however, gas, wood or charcoal is preferable for the foregoing purposes. Thus, in tempering machine guns, wood is used as fuel on account of its freedom from sulphur. The specific gravity of coke is from 1·2 to 1·9, rising with increased percentage of ash, but the texture of the fuel is so porous that this datum is but little guide to the space which the coke occupies in the furnace. In any case, ample room must be provided for its adequate combustion. Apart from the determination of ash and sulphur, the valuation of coke can be made by testing it by the calorimeter in the manner described for coal, and then its suitability must be judged by its texture and mechanical strength, according to the use to which it is to be put. Coke, on account of its comparative freedom from sulphur, its smokelessness, and the fact that in burning it neither fuses nor cakes, is used in place of coal for purposes in which any or all of these properties are desirable, in spite of its greater cost per heat unit.

BROWN COALS AND PEAT.—According to the age of the geological formation in which coal occurs, the character of the products of distillation of the coal varies. The older coals have been so far altered that the original grouping of the elements in the parent vegetable matter, which gives rise to acid products of distillation (see *Destructive distillation*—wood and peat, Vol. II.), has been modified, with the result that the products of distillation are alkaline from the presence of ammonia and other nitrogenous bases. Coals belonging to a later period have been less altered from the original composition of the woody matter from which they have been derived, and, like wood, yield a distillate containing acetic acid. Three classes of these later coals (*brown coals*) may be distinguished :—(1) **Brown coal,** with lustrous conchoidal fracture, is the oldest and most nearly related to ordinary bituminous coal. Handsome specimens of this substance are used for ornament as *jet*. A typical composition of the coal, free from ash, is about 75 per cent. C, 5 per cent. H, and 20 per cent. O, small quantities of nitrogen and sulphur being, as usual, present. (2) **Earthy brown coal,** of earthy fracture, as its name implies, containing in the ash-free coal 71·72 per cent. C, 5·76 per cent. H, and 22·50 per cent. O ; it is usually rich in ash and water. (3) **Ligneous brown coal** (*lignite*),* of fibrous fracture, showing a definite woody structure and containing 69 per cent. C, 5 per cent. H, 20 per cent. of O and N, and

* Some writers in this country misuse the word "lignite" to include all brown coals.

6 per cent. of ash. Brown coal, which is mined on a large scale in Austria and Germany, has a very variable calorific value on account of its fluctuating content of water and ash: 4,000 to 6,000 Cal. may be taken as ordinary limits. It burns with a considerable amount of flame, and is best used (especially the earthy variety) on *step-grates*—that is, grates with firebars arranged in a terraced form, as shown in the figure, which illustrates the system adapted to a kiln. *a* represents the masonry of the kiln. The steps of the grate are shown at *c c*. The ash falls on to the bottom of the furnace, *d*, whence it is removed, and the fuel is continuously fed so as to slide down the sloping set of firebars between which the air for its combustion enters.

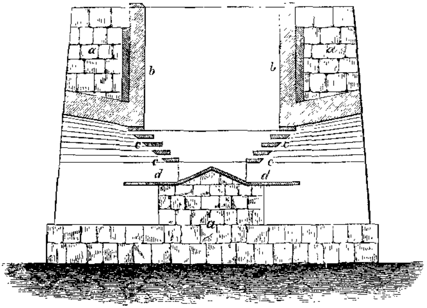


Fig. 5.—Kiln with step grates.

The most recent formation of a coal-like fuel is that exemplified by the peat bogs of Ireland and other countries. The change from fresh vegetable matter is not far advanced; the original material in this case is for the most part moss. The composition of **Irish peat** (free from water and ash) is about 60 per cent. C, 6 per cent. H, 34 per cent. O, and from 1 to 2 per cent. N. The ash varies from 5 to 15 per cent. of the dried material, but is occasionally much higher; speaking generally, it should not exceed 10 per cent. *Air-dried peat contains from 8 to 20 per cent. of* water, and the freshly cut material contains up to 80 or 90 per cent. of its weight of water. When air-dried its calorific value is from 3,000 to 5,000 Cal. The apparent specific gravity of peat

varies from 0·3 to 1·2, the real specific gravity being always greater than 1.

The volatile organic matter is usually between 50 and 70 per cent., and the fixed carbon from 10 to 25 per cent., calculated on the air-dried material containing 15 per cent. of water. Peat which has been pulverised and formed into blocks for use as fuel is termed "manufactured peat." During recent years the industry has been placed on a more intelligent basis, and the cheapness of its production on a large scale enables it in many localities to compete even with coal. Innumerable systems, differing mainly in their mechanical details, have been devised for the manufacture of these peat briquettes. The method is almost entirely automatic. An excavating elevator drops the raw material into a machine, in which it is disintegrated and kneaded into a plastic mass, which is cut up into pieces of a suitable size, pressed, and the slabs conveyed away to be dried, usually by air. Such a process costs from 3s. to 6s. per ton, according to local conditions. The air-dried slabs weigh from 40 to 60 lbs. per cubic foot (approximately the same as ordinary coal). An improved process for converting peat into fuel has been introduced during recent years. Its chief novelty lies in the method of expelling water from the raw material. This is done in a centrifugal machine, and a current of electricity is also made to pass through the peat. The current has a breaking up effect on the cells of the fibre, and allows a more free and perfect escape of the contained water. Such "electro-peat-coal" is hard, dense (75 lbs. per cubic foot), and comparatively smokeless.* Other methods have been tried in which the peat is treated with chemicals such as sodium carbonate and lime, so as to enable the moisture to be afterwards freed by pressure. These "chemical" methods, however, have not proved very successful commercially. Peat can be converted into coke in a manner similar to wood—*i.e.*, in heaps, kilns, and retorts. Modern processes, such as that of Ziegler, based on the simple dry distillation of the air-dried material are thoroughly commercial and satisfactory, and provide for the employment of the waste non-condensable gases and the saving of valuable bye-products. Peat coke is made and used in considerable quantity in Germany, Sweden, and other parts of the Continent, as well as in the West of England. It has a calorific value of about 6,000 calories, contains nearly 90 per cent. of combustible matter, and can be obtained sufficiently dense for metallurgical purposes. Its cost

* According to a report by Dr. Eugene Haanel, however, the product is hygroscopic, and has a tendency to crumble to powder. The process is, therefore, of doubtful utility.

is from 13s. to 16s. per ton, compared with 44s. for coke in the same place. The bye-products obtained in the destructive distillation of peat include (1) tar, from which is obtained oils, paraffin, and creosote; (2) watery liquids, such as acetic acid, ammonia, and naphtha; (3) gases for illuminating and heating purposes. The question of the utilisation of peat for gas-making and the production of cheap power is now being actively pursued. It has been proved that peat containing as much as 60 per cent. water can be used in special gas-producers, and a gas obtained which is suitable in every way for use in gas engines. Great reliance is placed on the value of the bye-products. About 80 per cent. of the nitrogen in the peat can be recovered as ammonium sulphate, at an estimated cost of £6 or £7 per ton. Experiments by Messrs. Crossley show that an output of 700 Board of Trade units can be obtained from 1 ton dry peat (= 10 tons wet peat) at a fuel cost of 0·05d. per unit, without crediting the profit on the bye-products.

An average analysis of dry producer gas from peat has been given as follows:—

CO,	= 12·0
CH_4,	= 2·8
H,	= 24·0
CO_2,	= 18·0
N,	= 43·2
	100·0

Peat producer gas has been used in the Swedish steel industry for a number of years, and is preferred to coal gas because of its low sulphur content.

In view of the anxiety which has been felt with regard to the supply of petrol for motive power (see p. 74), it is interesting to notice that a process has been worked out for the production of alcohol from peat involving its hydrolysis by dilute acids and fermentation with yeast. Useful bye-products are also obtained in the process, such as ammonium sulphate, creosote, and tar (see Sir W. Ramsay's Report in the *Automotor Journal*, July, 1907).

There are many uses for peat other than as fuel, but the discussion of them is beyond the scope of this book. They include the production of ammonia by moist oxidation (Woltereck process), the manufacture of nitrates, paper, wood, moss litter, and fodder (see *Commercial Peat*, by F. T. Gissing. London, 1909).

Briquettes.—Small dusty fuel, obtained as a bye-product in winning and sifting coal, can only be burnt in special forms of furnace—*e.g.*, those provided with continuous mechanical stoking apparatus, or with step grates (*v.s.*)—unless previously moulded

into blocks or briquettes which constitute so-called **patent fuel.** The fine stuff is washed and sifted, mixed with about 6 per cent. of pitch, tar, glutin or treacle, and moulded into bricks under a pressure of 5 to 10 tons per square inch. Brown coal has usually to be dried before it can be moulded, and can then be shaped without the addition of cementing matter, as the resinous substances which it contains are sufficiently cohesive at the temperature employed (75° C. = 167° F.).

Briquettes made with pitch soften at comparatively moderate temperatures, while those cemented with soluble binding materials are disintegrated by wet. An ideal binding material has still to be found. Improvements in mechanical stoking have recently permitted the use of much small fuel which was formerly practically a waste product.

WOOD AND CHARCOAL.—In this country wood is too scarce to find application as fuel, but it is largely burnt in lands still containing much forest. Wood free from water contains 50 per cent. C, 6 per cent. H, 42 per cent. O, 0·1 per cent. N, and 1 per cent. ash. Air-dried wood contains 15 to 20 per cent. of water; the content of water in freshly cut wood is from 20 to 50 per cent. Wood is not capable of giving a very high temperature when burnt, but it kindles more easily than coal, and burns with more flame. It has a calorific value (in the air-dried state) of about 3,000 Cal. Just as coal may be advantageously converted into coke, producing a non-flaming fuel, so can wood be carbonised to produce charcoal (see *Destructive distillation*, Vol. II.). The progressive change of wood to charcoal as the temperature of carbonisation increases is shown by the table below for the production of charcoal from black alder.

Temperature	C.	H.	O.	Ash.	Character of Product.
	Per cent.	Per cent.	Per cent.	Per cent.	
150° C. = 302° F.	47·51	6·12	46·29	0·18	Imperfectly carbonised.
200° C. = 392° F.	51·82	3·99	43·96	0·23	
270° C. = 518° F.	70·45	4·64	24·19	0·85	Brown charcoal.
350° C. = 662° F.	76·64	4·14	18·44	0·61	Black charcoal.
440° C. = 824° F.	81·64	1·96	15·24	1·16	
945° C. = 1,733° F.	81·97	2·30	14·15	1·60	
1,045° C. = 1,913° F.	88·14	1·41	9·26	1·20	
1,775° C. = 3,227° F.	96·52	0·62	0·94	1·94	

Brown charcoal, as might be expected, is more easily kindled than black charcoal. It is only used for the preparation of certain classes of gunpowder. *Black charcoal* increases in diffi-

culty of ignition as the temperature at which it has been carbonised rises. Good black charcoal has a calorific value of about 8,000 Cal. Its utility depends on its smokelessness and its freedom from smell and sulphur, on account of which properties it is used (on the Continent) for domestic heating, and in this country for fine metal work, stoving hops, and similar minor purposes.

B. **LIQUID FUEL—I. For Steam-raising.**—Liquid fuel is of minor importance in this country, as its price prevents its successful competition with coal for any but special purposes. It may be stated generally that liquid fuel has the advantage of being less bulky than coal for a given calorific value, of being free from ash, and of being more completely under control while burning, thus facilitating regulation of the fire, and, when used under a boiler, of the steam pressure. No stoking in the ordinary sense is requisite with liquid fuel, and, therefore, opening of fire doors

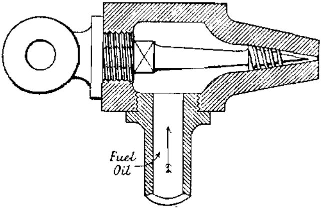


Fig. 6.—Körting injector.

and admission of cold air are avoided. The only successful methods of burning liquid fuel comprise the two plans—(1) feeding by natural flow down an inclined gutter; this is adapted for viscous liquids, such as tar; (2) injecting by an air or steam jet in the form of a spray. A "spray maker" of good design is the Körting injector, shown in Fig. 6. The oil is heated to 130° C. = 266° F., and forced into the injector under a pressure of 50 lbs. per square inch. The oil flows into a chamber leading to the jet, in which chamber is placed a spindle carrying a spiral screw. The oil is forced down this spiral, and acquires a centrifugal motion which sprays it out of the jet in a finely-divided condition. In the Orde system, the oil flows through a settling tank, in which water and other impurities separate, and is then passed to the burner under a pressure of 60 lbs. to the square inch. On its way it is heated by the waste heat of the burnt

gases, and on emerging from the inner tube of the burner, at a temperature only just below its boiling point, the oil is met by a jet of air and steam-heated to 316° C. = 600° F. or more, and wholly converted into vapour. For marine purposes, the report to U.S. Naval Liquid Fuel Board of 1904 recommended that only those burners should be used which are capable of vaporising the oil without the aid of steam or compressed air. In this country, tar and creosote oil (dead oil: see *Coal Tar*, Vol. II.) are used to a small extent, as well as astatki imported from Russia, and heavy American oils. As far as Russia is concerned the petroleum still residue, *astatki* (see *Petroleum*, Vol. II.) is employed. The ultimate composition of the materials used as liquid fuels is similar for all kinds. Thus, taking the combustible constituents, tar contains about 85 per cent. C and 5 per cent. H; creosote oil 83 per cent. C and 10 per cent. H; astatki 85 per cent. C and 10 per cent. H. Astatki and similar petroleum products have a calorific value of about 11,000 Cal., as compared with 8,000 to 9,000 for good steam coal; the other liquid fuels give slightly lower values. It will be seen that astatki is the best liquid fuel, but it cannot be remuneratively imported into this country. Once-run Russian petroleum (*q.v.*) is imported for gas-making, but can barely compete with creosote oil. Crude petroleum is not imported for use as liquid fuel, both on account of the danger of transporting and handling a material containing constituents of low flashing point, and also because it is more profitably distilled fractionally to obtain lighting and lubricating products. Of definite products of fractionation, none but the residue is cheap enough for use as fuel. Astatki, freed only from about 30 per cent. of the more volatile constituents, is now the chief product obtained from Russian petroleum. Similar conditions prevail in California and Texas. In the injection process for burning liquid fuel, mentioned above, the function of the jet of steam, when this is used, is purely to "atomise" the oil, for it obviously cannot be supposed, as has been ignorantly stated, that the steam contributes to the heating effect of the fuel. Any heat from the combustion of hydrogen with oxygen which may be obtained by the dissociation of the steam, is exactly counterbalanced by the absorption of heat previously needed to effect the dissociation.

Where compactness in storage is important—*e.g.*, on board ships of war—the small bulk of liquid fuel presents a notable advantage. One ton of liquid fuel occupies about three-quarters the volume occupied by a ton of coal, and as its heating efficiency is one and a-half times that of an equal weight of coal, it follows that the liquid fuel requisite for a given horse-power

takes up about one-half the space required by coal for the same output. All the larger vessels of the British Navy are now fitted to burn liquid fuel as well as coal, whilst some of the later destroyers burn liquid fuel exclusively, in combination with water-tube boilers and turbine engines. Russia has for some time used astatki in her warships, and the U.S. are about to employ liquid fuel in destroyers. A disadvantage appears to be that with the limited furnace space available in marine boilers, dense smoke may be emitted under forced-draught conditions when liquid fuel is used. Attempts have been made to prepare liquid fuel in a form capable of use in an ordinary furnace. Two methods of "solidifying" petroleum have been devised for this purpose. The first depends on the fact that when soap is added to an unsaponifiable oil, such as petroleum, the whole mass becomes gelatinous, not from any chemical action on the petroleum, but simply from the property of soap of forming an apparently homogeneous jelly with many liquids, water being a case in point. The jellies of the greatest consistency are made by forming the soap *in situ* by adding a saponifiable oil or a fatty acid to the petroleum and then the requisite amount of alkali. The jellies made by the aid of castor oil and coco-nut oil are particularly firm and coherent. The second plan for solidifying petroleum consists in absorbing the liquid by a porous material in the manner in which nitroglycerin is solidified by absorption in kieselguhr (see *Explosives*, Vol. II.). Since siliceous matter of this kind would remain on combustion as ash, some combustible material, such as cheap vegetable fibre—*e.g.*, peat—is to be preferred. Solidification by means of a material of this nature may be aided by the addition of soap. Products of both types are liable to ooze in the furnace before igniting thoroughly, and their stability when stored in hot places is also doubtful. The fact that Russian petroleum contains naphthenes, which are capable of oxidation to acid products by air in the presence of sulphuric acid, makes it possible that should a demand arise for solidified petroleum it may be prepared by saponifying such acid substances *in situ*. (The production of soap from acid oxidised products of petroleum has, however, not yet been accomplished on a commercial scale.) The adoption of "solidified" liquid fuel on a considerable scale is improbable, as by the solidification the advantages obtained by the use of liquid fuel are sacrificed, and a direct comparison with coal becomes even more favourable to the latter.

II. For Internal-combustion Engines.—Of greater importance, so far as this country is concerned, than its use under the boilers of steam engines, is the application of petroleum to the direct

provision of energy for conversion into mechanical power by explosive combustion in the cylinder of an oil engine For this purpose, *petrol* is largely used. Petrol is a low boiling fraction of petroleum, of specific gravity 0·70 to 0·74, with a calorific value of about 11,200 Cal., or 20,160 B.T.U. It volatilises so readily at the ordinary temperature that its vapour can be mixed with air in an apparatus termed a "carburettor," and introduced in this manner into the explosion cylinder. The proportion of petrol vapour taken up by the air may vary between fairly wide limits, from about 1·1 to 5·3 per cent. The thermal efficiency—*i.e.*, the heat converted into useful work—is commonly about 18 per cent., but under favourable conditions and with large engines may be as high as 25 per cent.

The portability of petroleum, as compared with compressed gas even of the richest kind (oil gas), and the practicability of directly utilising its energy for the production of mechanical power, are valuable properties which are taken advantage of in the case of launch engines, and in isolated places where power is wanted without the risk attendant on trusting a boiler to unskilled hands, and where gas is not available. The most important use of petrol engines is for the propulsion of vehicles on land, but such engines are also largely used on pleasure boats. Submarines are worked entirely by petrol, directly when on the surface, and indirectly when submerged, through electrical energy previously generated by the petrol engine, and stored up in accumulators. The motors of flying-machines, both of the dirigible balloon and aeroplane type, are driven by petrol. The compressed air used in driving torpedoes is heated (*i.e.*, energy is imparted to it) by the combustion of petrol (*cf.* p. 79). With regard to the chemical aspect of this utilisation of liquid fuel, it may be said that petrol shonld be a fairly homogeneous fraction of petroleum—*i.e.*, it should distil within narrow limits in order that the rate of volatilisation may be uniform, and that no residue of heavy difficultly volatilised oil may be left in the vessel in which the air is "carburetted" before explosion. Similarly, kerosene should be free from acid (due to careless refining), and from heavy fractions tending to condense and carbonise at the moment of explosion. It may be added that the variable character of commercial oils renders it desirable that they should be systematically examined to ascertain whether they comply with the limits specified.

In cases where gas is not available, and solid fuel is inconvenient, petroleum (both gasolene and kerosene) is used directly for heating either as carburetted air (see also *Oil air-gas*, p. 75), or burnt from a wick; portable experimental

and assay furnaces have been constructed to use liquid fuel in this manner.

The increasing demand for petrol for motor use led to a marked increase in price, and to anxiety regarding a possible "petrol famine." A good deal of this increase of price was, however, artificial, and has abated under competitive conditions. But as petrol constitutes only about 5 per cent. of total crude petroleum, and must be looked upon as a bye-product, the production of which is regulated by the demand for the other fractions, a constant low price is not to be expected. These considerations have led to a search for other liquid fuels capable of use in internal combustion engines. Three such liquid fuels have been proposed, paraffin, benzene (benzol), and alcohol. All three, being less volatile than petrol, present difficulties in starting: when the engine is once running, the exhaust gases may be utilised to warm the carburettor.

For **paraffin,** carburettors are generally used in which the liquid is "atomised," and the sprayed liquid mixed with the air with which it is to be exploded. The range of composition over which the mixture remains explosive is less with paraffin than with petrol: hence a mechanical and accurately measured feed is inevitable, and the load cannot be varied easily. The specific gravity of paraffin is about 0·80 to 0·85, and its calorific value 10,990 Cal., or 19,782 B.T.U.

The production of **benzene** is strictly dependent on that of the coal-tar from which it is derived (see Vol. II.), and benzene is even more definitely a bye-product than petrol itself. Its calorific value is lower than that of petrol, being 10,050 Cal., or 18,090 B.T.U. Its specific gravity is 0·885. Good results have been obtained when using benzene mixed with petrol or alcohol, but so far it has not been used in practice by itself.

Alcohol is used to a considerable extent on the Continent, especially for agricultural motors. Its use is encouraged by several foreign Governments, since alcohol is produced from beet or potatoes, and thus constitutes a home-grown product, as distinct from imported petroleum. The calorific value of alcohol is low, 7,000 Cal. for pure ethyl alcohol, 6,300 Cal. for methyl alcohol, and about 5,500 Cal. for the denatured 80 per cent. alcohol largely used. The thermal efficiency, on the other hand, is high, being about 30 to 35 per cent. It is stated that with alcohol engines a more uniform pressure is obtained than with petrol engines. The difficulty of first starting the engine has been more or less overcome by the use of special devices, and the calorific power has occasionally been increased by adding benzene (*v.s.*).

Oil-air Gas.—This gas has recently been used for lighting and heating country houses in isolated places, etc. It consists simply of air mixed with a small proportion of petrol vapour. In order to effect the mixture, a fan driven by a small hot-air engine, worked by a part of the gas produced, blows air over the surface of petrol contained in a carburettor. The petrol is warmed by the water from the cooling jacket of the hot-air engine. The air takes up petrol vapour, and passes to a small mixing chamber, into which the fan blows a further quantity of air, so as to reduce the percentage of petrol vapour in the mixture to about 1·5 per cent. The gas is stored for use in a small gasholder, the rise or fall of which governs the relation between the quantity of air sent into the carburettor and that forced directly into the mixing chamber. The gas obtained must be burnt from special burners containing a number of wire-gauges to ensure perfect mixing; the gas will not ignite if allowed to issue from a hole in the pipe or from an ordinary burner.

C. **GASEOUS FUELS.**—With the exception of natural gas (*q.v.*) all gaseous fuel is prepared artificially, and its preparation involves the consumption of rather more energy than appears in the product in an available form, since the usual inevitable loss attending the conversion of energy must occur. Thus coal can be either burnt as solid fuel, or completely gasified and then burnt. Taking into account the energy necessary for the gasification, the gasified coal must contain less total energy than the coal when solid, and no gain of energy can possibly take place. Nevertheless, it often happens that the advantages of gaseous fuel outweigh commercially the loss of energy involved in its formation, and the efficiency actually obtained with gaseous fuel may be greater than if the corresponding quantity of solid fuel had been burnt directly. The main advantages of gaseous fuel of all kinds will be evident from the following considerations:—

1. Gases can be readily, rapidly, and perfectly mixed, and thus the quantity of air exactly adjusted to that of the gas to be burnt, whereas solid fuel, burning exclusively at its surface, needs excess of air in order that its combustion may be complete, and the formation and final escape of imperfectly oxidised products—*e.g.*, CO—avoided. Were it possible to allow the air to remain in contact with the burning solid fuel until the reaction between them became complete, no excess of air beyond the calculated amount would be requisite, but under practical conditions the necessary sojourn would be unduly lengthy, and incompatible with the conditions necessary for continuous combustion. In gaseous firing, therefore, the restriction of the air

supply to a small excess over the calculated quantity diminishes the weight of the final flue gases, as compared with those given by solid fuel, and consequently, for a given temperature of escape, decreases the quantity of heat which they carry away.

2. Firing with gaseous fuel can be regulated with the same ease as that already mentioned as characteristic of liquid fuels, and in addition can be used with excess or defect of air as may be desired, to yield an oxidising or a reducing atmosphere.

3. Freedom from ash and soot, a matter of importance for many industries, is secured by gaseous firing.

4. Gaseous fuel adapts itself readily to the use of regenerative heating, and thus lends itself to the production of high temperatures.

5. Small fuel, containing much ash, and bulky fuel—*e.g.*, peat—are more readily dealt with by preliminary gasification than by direct burning.

6. Gaseous fuel is a very convenient source of power when burnt in the gas engine, and thus provides an alternative to the use of the steam engine with its very low efficiency.

Gaseous fuel can be produced from solid fuel by processes which may be divided into two classes—(*a*) destructive distillation involving the formation of a fixed carbonaceous residue, and (*b*) complete gasification with the removal of the whole of the fuel (with the exception of the fixed mineral constituents) as gases.

COAL GAS, which is the only gas made by destructive distillation, and distributed on a large scale, is not primarily prepared for heating and as a source of power, but it is nevertheless used as a domestic fuel and for supplying moderate quantities of mechanical energy by means of the gas engine as intermediary. Its production and composition are described in the section on *Destructive distillation*, Vol. II.

For the production of heat as a warming and cooking agent it is burnt in two distinct ways—(1) from jets or slits giving a luminous flame (with or without a chimney), and (2) from burners of the bunsen or "atmospheric" type, in which it is mixed with air at a point anterior to that at which it is burnt. The total calorific effect is constant, however the gas is burnt, provided its combustion be complete. Choice between the methods turns on their convenience under given conditions. For rapid heating in contact with the flame—*e.g.*, boiling—the non-luminous flame is necessary, as it does not deposit soot on the vessel heated, which would form a non-conducting layer. Soot thus deposited also obviously means the loss of fuel. Where heating by radiation is contemplated, the gas may be burnt with a luminous flame, preferably with the aid of a chimney, as in an argand burner (the

total radiant heat being then about 12 per cent. of the total chemical energy of the gas). In such cases the products of combustion are only as deleterious as those of ordinary unprotected gas jets used for lighting purposes, and a flue may sometimes be dispensed with in a well-ventilated room. For burners of this type used for heating rooms, an arrangement to condense the water produced by the combustion of the gas is sometimes provided, and undue moistening of the air of the room thus avoided. but the CO_2 and other gaseous products of course escape. Heating by radiation may also be effected by the use of a non-luminous flame caused to heat a refractory material—*e.g.*, iron, platinum, asbestos, or fireclay—to incandescence. With such stoves a flue should always be used, as at the cooler parts of the material to be heated, combustion is checked by contact of the flame with a solid body, and the usual products of checked combustion—among which are acetylene and carbon monoxide, gases of markedly toxic properties—are formed. Evidence of such checked combustion is given by the sense of smell in the air of a room in which a kettle of water is being heated over a common burner of the bunsen type. Even when coal gas is burnt from the best form of heating or lighting burners which have no device to carry off their products of combustion, the air of the room is liable to serious contamination. Thus each cubic foot of ordinary coal gas yields about 1 ounce of water and 0·57 cubic foot of CO_2. As a common flat-flame burner consumes about 5 cubic feet per hour, the quantity of the main products of combustion becomes considerable in a well-lighted room. The amount of SO_2 produced per 100 cubic feet of gas burnt is about 40 grains. The effect of these products of complete combustion is enhanced by that of unoxidised or imperfectly oxidised products, hydrocarbons and CO, which invariably appear in small amount. The percentage of CO_2 in normal air is 0·03 per cent., and the approximation to normal condition of the air of a given room is generally gauged by its contents of CO_2. This should not be above 0·1 per cent., but is frequently exceeded when much gas is burnt. It is doubtful whether it has any toxic effect, being merely non-supporting of life. Carbon monoxide, on the other hand, is distinctly poisonous, but the question of its presence in coal gas becomes of importance only when an escape of unburnt gas (which contains about 6 per cent. of CO) has occurred (see *Water gas*).

The calorific value of coal gas averages 170 Cal. per cubic foot —*i.e.*, 673 British thermal units.* The chemical energy of coal gas can be directly converted into mechanical work by means of the gas engine. In this machine a mixture of gas and air (1 volume

* This represents about one-fifth of the calorific value of the parent coal.

gas with 9 to 11 volumes air) is exploded behind a piston, and the longitudinal motion thus imparted to the piston converted into circular motion as in a steam engine. The use of a sudden and violent impulse, such as is implied in the word "explosion," does not on *a priori* grounds recommend itself as an economical method of obtaining power, but it must be understood that the explosion is of a more gradual kind, on account of the dilution of the charge and the rapid enlargement of the chamber in which it takes place (due to the advance of the piston) than that characteristic of a shattering explosion produced by a blasting explosive. There is a difference in degree, but not in kind, between the ignition of a gas engine charge and that of a rifle or piece of artillery, the propulsive effect in some of the larger guns partaking of the nature rather of a steady, though extremely vehement, push than of a violent shock. Another cause for the gradual character of the impulse in a gas engine, is the prevention of instantaneous and complete explosion of the mixed gases in its cylinder by the raising of their temperature, owing to an explosion of part of them, to the temperature of dissociation of their products of explosion, inhibiting further combination. As the piston moves the gases expand, doing work, and their temperature falls, allowing fresh combination of unused portions, until the dissociation temperature is again reached. The process of explosion is, therefore, automatically controlled, continuous and steady, and the power is exerted fairly uniformly during the stroke.

The gas engine, though more efficient than the steam engine, still leaves a good deal to be desired. The average output of mechanical work corresponds with 20 to 25 per cent. of the energy present in the coal gas. This low result is largely caused by the necessity for cooling the working cylinder (by means of a water-jacket). The necessity arises from the difficulty of finding a lubricant which will both retain a fair degree of viscosity (see *Lubricants*) and not suffer decomposition at high temperatures. Another reason for cooling the cylinder is the decreasing strength of structural materials (metals notably) with rise of temperature. A third reason for cooling lies in the danger of pre-ignition during the compression stroke, especially when gases rich in hydrogen (water-gas, coal-gas) are used. It is obvious that a large fraction of the energy of the exploded gas goes to warm water instead of performing mechanical work. Combustion in a gas engine is usually nearly complete,* but an exhaust into the open air is,

* Combustion in an oil engine is also nearly complete, but a good deal of waste is often occasioned by imperfect spraying, oil being ejected in drops with the exhaust.

of course, as necessary as with a gas stove. The economical consumption of coal gas in a gas engine is seldom of great importance, as for larger powers, where the cost of energy, apart from other charges, becomes a tangible item, coal gas is not used, producer gas (*q.v.*) being substituted for it.

There is another use of coal gas as a source of energy which requires comment—viz., the supplementing of the effect of compressed air, supplied from central stations as a motive power in a few cities. The air before entering the motor is heated by a gas burner, and thus the energy represented by the motion of its molecules is increased, and risk of condensation and freezing from undue cooling during the expansion of the compressed air while working is avoided. In estimating the efficiency of any system of this kind of distributing energy, the energy imparted directly as heat must naturally be taken into account. Another minor use—*e.g.*, in laboratories largely using electrolytic methods—consists in heating thermo-electric batteries by gas jets, and storing the current thus obtained in accumulators. The system is extremely wasteful from the point of view of the output of electrical energy obtained for a given expenditure of chemical energy, but has convenience to recommend it.

Coke-oven gas is one of the bye-products of the manufacture of coke for metallurgical purposes. Its composition is similar to that of coal-gas, but the gas is somewhat richer in methane and considerably poorer in hydrogen. The average calorific power is about 620 B.T.U., or 156 Cal. per cubic foot. At present, much of the gas produced, beyond that required to heat the ovens, is burnt to waste. Where the gas can be sold, it is economical to collect it in two portions. A rich illuminating gas (3,000 to 4,000 cubic feet per ton of coal) during the first stage of heating, and a poorer power gas (5,000 to 6,000 cubic feet) during the second stage.

Coalite is coal deprived of a portion only of its volatile matter. It has been introduced as a smokeless fuel for domestic grates, *in which it produces a more cheerful fire than does coke. Coalite* is made by heating bituminous coal under moderate pressure in retorts, a temperature of 427° C. (800° F.) being gradually attained. As soon as no more gas is produced, the residue is cooled by introducing steam. The gas given off contains an appreciable quantity of ethane, which is not present in ordinary illuminating gas. Its calorific value is high, but its illuminating *power low. At Wednesbury the gas is* used *for the manufacture* of ferro-silicon in the electric furnace.

GENERATOR GAS.—By this term is meant gas made by the second method defined above—viz., that method by which

complete gasification of the fuel is effected. There are three main kinds of generator gas—(1) *producer gas* made by the limited action of air alone on fuel; (2) *water gas* made by the action of steam upon heated fuel; and (3) *semi-water gas* made by the action of both air and steam upon fuel. Gases of the type of water gas and semi-water gas can be made by the action of CO_2, alone or mixed with air, upon fuel.

(1) **Producer Gas.**—The first of these (producer gas) has carbon monoxide as its chief combustible constituent, and its formation depends primarily on the production of carbon monoxide when carbon is burnt in a limited amount of air, the ultimate result being expressed by the reaction—

$$C + \underbrace{O\ (+ N_4)}_{\text{Air.}} = CO\ (+ N_4).$$

It is usually considered that the production of CO from carbon and a limited supply of oxygen (or air) proceeds in two stages, thus:—

$$(1)\ C + O_2 = CO_2.$$
$$(2)\ CO_2 + C = 2CO.$$

According to this view, air on first entering a producer combines with the carbon of the fuel to form CO_2, and this passing up through the mass of hot fuel is reduced to CO, which constitutes the chief combustible constituent of producer gas. It has been stated, however, that carbon at a temperature of 1,000° C. = 1,832° F. unites directly with oxygen to form CO, no intermediate formation of CO_2 occurring. Considerable doubt exists as to whether this is so, and whatever the mechanism of the change the ultimate result is the same—viz., the conversion of solid carbonaceous fuel into the gaseous fuel, CO. The formation of CO by the limited oxidation of C evolves a large quantity of heat, and the main reaction concerned being thus powerfully exothermic, the continuous formation of producer gas without the aid of external heat is easy. A modern form of gas producer is shown in the figure. The producer consists of a combustion chamber, A, into which the fuel is fed through the hopper, B; it suffers limited combustion by the air entering through the flue, C, and the distributor, D. The producer gas is led off by the flue, E, and the ash and clinker of the gasified fuel are continuously removed by the conveyor, F, which rotates under water, the latter serving to seal the producer chamber. The clinker is forced out at the shoot, G. In general the air is either drawn in by the draught of the stack of the furnace, which

is fed by the gas from the producer, or is blown in by injectors.*

As in practice, coal (and not coke) is generally used in a producer, reactions subsidiary to the main chemical change (viz., the production of CO) take place. The mere heat of the combustion chamber suffices to destructively distil a portion of the coal, the residual coke being afterwards gasified by limited combustion. Thus it happens that a certain amount of hydrocarbons appears

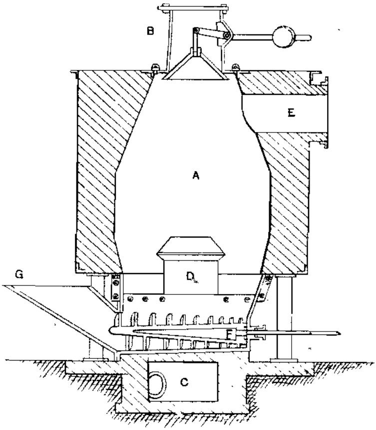


Fig. 7.—Gas producer.

B, Hopper; C, E, flues; D, distributor; F, conveyor; G, shoot.

in ordinary producer gas. The composition of pure producer gas (from carbon only) and that of the ordinary product are given on the following page.

* In the particular producer here figured the air is forced in by a steam injector, so that the product is semi-water gas as opposed to pure producer gas (*v.i.*).

	Pure Producer Gas.	Actual Sample.
	Per cent.	Per cent.
CO,	34·4	22·8
N,	65·6	63·5
CO_2,	...	3·6
H,	...	2·2
CH_4,	...	7·4
O,	...	0·5
	100·0	100·0

Average producer gas has a calorific value of about 28 Cal. per cubic foot—*i.e.*, about 111 B.T.U. The total amount of chemical energy (as distinct from sensible heat) in the gas thus produced from a given weight of coal is about ⅘ that in the coal. The fulfilling of the reactions involved in the complete oxidation of C causes the following thermal changes :—

$$(1)\ C + O = CO + 29{,}000\ \text{Cal.}$$
$$(2)\ CO + O = CO_2 + 68{,}000\ \text{Cal.}$$

This means that 12 kilos. of carbon when oxidised to carbon monoxide evolve 29,000 Cal., and when the resulting carbon monoxide is oxidised to carbon dioxide a further evolution of 68,000 Cal. occurs. Therefore, in the preparation of producer gas a large fraction (nearly ⅓) of the total energy available from the oxidation of the carbon appears as sensible heat in the producer. Unless, therefore, the producer gas can be used close to the producer, so that it is but little cooled by the time it reaches the point of combustion, a waste of ⅓ the total energy of the fuel is incurred. The sensible heat of producer gas can, however, be rendered latent and available at a distance in one of several ways, of which the manufacture of semi-water gas serves as a type (*v.i.*).

In all systems of heating by fuel (as opposed to direct electrical heating) great difficulty is experienced in utilising the heat in the products of combustion after their temperature has fallen to a certain minimum. Thus, when there is no feed-water heater (applicable in the case of a boiler) or other economising arrangement, the temperature of the issuing gases may be 600° to 700° F. = 315° to 371° C. The heat thus escaping to the chimney amounts to about 20 per cent. of the whole heat evolved by the combustion of the fuel. It is found to be impracticable in most cases, even when the substance to be heated has to be raised to only a moderate temperature (*e.g.*, the water in a boiler which may have to be heated only to 300° to 400° F. = 149° to 204° C.)

to utilise the heat of the products of combustion directly, when their temperature has fallen below 600° F. = 315° C. A certain residuum of heat in the flue gases has to be left to afford a draught, unless some system of forced draught be used. Nevertheless, a large amount of waste occurs in any system of firing in which no special provision exists for turning low temperature heat to account.

Several methods exist of **utilising the low temperature heat** of products of combustion which have accomplished their main work of heating. They differ according to the nature of the industry using the main source of heat. Thus, in industries where evaporation has to be effected, waste gases are made to pass underneath the evaporating pans; the evaporation of tank liquor in the Leblanc alkali process (*q.v.*, Vol. II.) is a case in point; where moist materials have to be dried, as in drying slurry for cement making, a similar method of economy is practised; where feed water has to be heated for steam-raising the gases pass through an economiser which consists of a number of vertical iron tubes through which the feed water flows, and round which the boiler gases—*i.e.*, the products of combustion from the boiler grate—circulate. A use of a different kind, specially advantageous when high temperatures have to be produced, consists in heating the air supply before combustion by the waste heat of the furnace gases. Thus, it has been found economical to heat the air supplying a series of boilers by passing it through iron tubes set in the furnace flues, and, therefore, heated by the furnace gases.* This method of pre-heating the materials to be burnt is particularly applicable to gaseous firing, as both the fuel and the air can be heated, instead of the air only, as in the case of solid fuel. High temperatures can be easily obtained by employing a system of "regeneration" such as this. A regenerator is shown in the figure, the top portion of which represents a vertical section through a combustion chamber, A (in which is the substance to be heated—*e.g.*, steel), and the regenerators B, C, D, E, whilst the lower portion of the figure is a ground plan of the flues through which producer gas and air are fed to the regenerators. The method of operation is as follows:—When the furnace is at work, the products of combustion leave the combustion chamber, A, by way of the regenerators D, E, which contain chequer work of firebrick to which the hot gases impart a large portion of their heat; they then pass away through the flues, a_1 and g_1 (which are shown in the ground plan in the lower portion of the figure), and thence

* Yet another method consists in superheating steam from a boiler on its way to the cylinder by passing it through tubes set in the flues.

to the chimney of which the entrance is shown at F. From the same plan it will be seen that the producer gas and the air necessary for its combustion pass through the flues g and a, and thence up the regenerators B and C, shown in the section. When the firebrick in the regenerators D and E has been heated until the temperature of the upper end of the regenerators (nearest

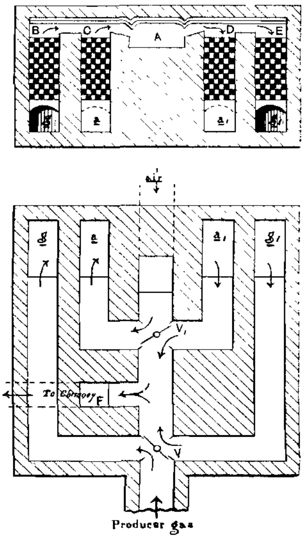


Fig. 8.—Regenerator.

A, Combustion chamber; B, C, D, E, regenerators; a, g, flues; F, entrance to chimney; V_1, V, valves.

the combustion chamber) approaches that of the furnace, the valves V_1 and V are reversed, so that the air and producer gas now flow through the flues a_1 and g_1, and pass through the

chequer work in the direction reverse to that previously taken by the products of combustion, and are thereby heated before they reach the combustion chamber. It is now the turn of the regenerators B and C to become heated by the products of combustion which pass away through the flues, *g* and *a*. It will be seen that the whole working is systematic—*i.e.*, the cold gases enter the cooler end of the regenerator and leave at the hot end, whilst the hot products of combustion enter at the warmer end of the regenerator and leave at the cool end. In this case the same canal serves alternately to absorb heat from the products of combustion, and to impart heat to the gases to be burnt; it is obvious that the hot products of combustion and the cold combustible gas (or air) can be passed simultaneously in reverse directions through parallel canals separated by a septum capable of transmitting heat; an arrangement of this sort is shown under the head of destructive distillation of coal (*q.v.*, Vol. II.), and a simple instance thereof is afforded by the regenerative system applied to steam boilers for utilising the heat of their furnace gases, which has been already mentioned (p. 83).

The regenerator is applicable not only to producer gas, but to the other qualities of gaseous fuel about to be described. The principle in all cases is the utilisation of what would be waste heat for the preliminary heating of the materials about to be burnt. It should be said that, in general it is more important to pre-heat the air needed for combustion than the gas, since the quantity of the former is greater than that of the latter. Pre-heating of the gas is also troublesome, since contact with oxygen must be avoided in the regenerators.

Since heating by radiation generally results in a more gradual and uniform rise of temperature than heating by contact, methods have been devised for causing a luminous flame to play across the arch (the top of the chamber A, Fig. 8) of a regenerating furnace, so that the material—*e.g.*, plate glass to be softened—may be heated by radiation from the white hot particles of carbon in the flame, and not by contact with the hot gases constituting the flame. Such a luminous flame is obtained by careful adjustment of air and producer gas supplied to the furnace.

Fairly successful attempts have recently been made to utilise low-temperature heat by means of sulphur dioxide engines. These are similar to ordinary steam engines in principle, but liquid sulphur dioxide takes the place of water. The temperature of the liquid being raised by the hot flue-gases which surround the "boiler," it evaporates, expands, and does work, the gas escaping at the end of the stroke into a condenser, whilst still

under sufficient pressure to cause it to return to the liquid state on cooling to the ordinary temperature. The liquid is then returned to the boiler.

2. **Water Gas.**—By this term is meant the gaseous mixture, consisting essentially of CO and H, which is produced by the action of heated carbon upon steam. The reaction appears to take place in two stages, thus—

$$(1)\ C + 2H_2O = 2H_2 + CO_2.$$
$$(2)\ C + CO_2 = 2CO.$$

As in the case of producer gas (*v.s.*), it is stated that carbon may be oxidised directly to CO at temperatures above 1,000° C. = 1,832° F., thus—

$$(3)\ C + H_2O = H_2 + CO.$$

In the case of equation (1) 12 kilos. of carbon in being oxidised by steam require to bring about the reaction an expenditure of 18,200 Cal.: similarly equation (2) requires 39,000 Cal.; equation (3), therefore, needs half the sum of these values—viz., 28,600 Cal. In these cases the water is already in the form of steam, but when liquid water is the starting point for calculation, the quantity of heat needed is necessarily greater by the amount necessary to convert the water into steam—*i.e.*, 10,800 Cal. Seeing that the occurrence of the fundamental reaction, $H_2O + C = H_2 + CO$ for the production of water gas involves the absorption of 28,600 Cal. even when the water is already in the form of steam, it is obvious that any system of manufacture must be designed to communicate a large supply of heat to the raw materials, C and H_2O. A plan for supplying this heat, which has the apparent merit of simplicity, would consist in heating a vessel containing solid fuel from without, and blowing steam through it. The method is impracticable on account of the cost of transmitting the heat through the walls of a suitable vessel, such as a gas retort. The device actually adopted consists in obtaining the necessary amount of heat by the oxidation by air of a portion of the fuel which is to be gasified. This is effected by blowing air into the bottom of the generator containing the fuel (as shown in Fig. 9), and thus making producer gas (carbon monoxide and nitrogen), which passes away by the flue on the right of the figure, heat to the extent of 29,000 Cal. per 12 kilos. of carbon burnt being at the same time evolved. When the interior of the producer is thus highly heated, the air is cut off and steam is blown into the upper part of the generator, forming carbon monoxide and hydrogen, until the heat absorbed by this reaction lowers the temperature below that necessary for its occurrence.

The steam passes down the hot column of fuel, its action being thus systematic, and the water gas is led away through the pipe as shown. The first part of the process (admission of air) is called the **hot blow**, and the second (injection of steam) the **cold blow.** It will be seen from equation (3) that ideal water gas should contain 50 per cent. H and 50 per cent. CO (by volume).

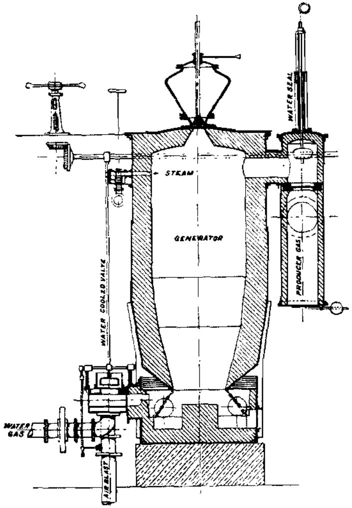


Fig. 9.—Water gas producer.

In practice, however, a certain amount of producer gas, formed during the hot blow, is mixed with the water gas proper resulting from the cold blow. The average composition of water gas is—CO, 41 per cent.; H. 48 per cent.; CO_2, 6 per cent.; N, 5 per cent.—by volume. The producer gas formed during the hot blow has the usual composition (*v.s.*), and is utilised for steam-

raising and various heating purposes, such as the "fixing" of hydrocarbons when the primary object of the preparation of water gas is the production of a carburetted gas for enriching common coal gas. Where high temperatures are especially needed, water gas is a better, because more concentrated, fuel than producer gas, but its economical employment depends largely on a use being found for the producer gas which is made as its bye-product. Average water gas has a calorific value of 291 B.T.U. per cubic foot—*i.e.*, 74 Cal. When fuel is gasified by this duplex system, the total quantity of chemical energy in the two gaseous products (producer gas and water gas) amounts to about 77 per cent. of that in the fuel (coal or coke) used.

In the Dellwik and Fleischer process, producer gas is not made. By reducing the layer of fuel, and maintaining a very rapid air-blow for a short time only, the carbon is burnt to carbon dioxide during this period. Consequently less carbon is used to furnish the heat needed during the cold blow, and practically no CO is produced. The calorific value of the water-gas so obtained is 319 B.T.U. per cubic foot—*i.e.*, 80 Cal. The gas is stated to contain about 82 per cent. of the chemical energy of the coal.

3. **Semi-water Gas** (Dowson gas).—This form of gaseous fuel is produced by injecting *simultaneously* air and steam into a producer. The air forms with the fuel producer gas, this process evolving heat; the steam reacts with the fuel to yield water gas, the process absorbing heat. By regulating the proportions of air and steam the temperature of the producer may be kept sensibly constant and a gas obtained consisting of a mixture of producer gas and water gas. The apparatus used for making semi-water gas is simply an ordinary producer, such as is figured in the section on producer gas, provided with a steam injector. It has been indicated above that a common producer only works to advantage when it is situated in close proximity to the furnace which it is supplying, the gas thus reaching the furnace without notable loss of sensible heat. If the connecting pipe be long, much cooling occurs and a large loss results. When instead of the energy appearing as sensible heat in the producer gas, it is converted into potential chemical energy by manufacturing semi-water gas, the distance of the producer from the furnace is of minor importance. Supposing that the whole of this heat were utilised in the production of water gas, the semi-water gas would contain 58 per cent. of ideal producer gas and 42 per cent. of ideal water gas, and consist of H, 21·1 per cent.; CO, 40·9 per cent.; N, 38 per cent. Semi-water gas as actually made falls considerably short of the ideal composition

containing about H, 15 per cent.; CO, 27 per cent.; CH_4, 2 per cent.; CO_2, 4 per cent.; N, 52 per cent. It has a calorific value of about 41 Cal. or 163 B.T.U. per cubic foot.

One of the chief uses of semi-water gas is as a source of power in the gas engine (*v.i.*). For this purpose it must be free from tar and hydrocarbon vapours, so as not to clog the pipes and taps leading to the engine. Consequently, especially for the smaller power plants, coke or anthracite is used in the producer, and not bituminous coal, as the lower price of the latter is more than counterbalanced by the cost and inconvenience of having to purify the gas obtained. A number of producers have, however, been constructed to work with bituminous fuel; in all these the tarry vapours given off by the green fuel are forced to pass through the mass of incandescent coke in the producer and are thus converted, to a greater or less extent, into "fixed" gases. This "fixing" may be effected by blowing the air and steam downwards through the fuel in the producer, and drawing off the gas at the bottom; or by the method adopted in the Mond producer (*v.i.*); or else, as in the Loomis-Pettibone process, by working two producers alternately, the two producers being connected together at the top, and provided with separate gas outlets and air and steam inlets at the bottom, in such a way that the gases given off by the fresh charge of coal at the top of the producer which is being blown must traverse the hot fuel in the second producer, which has just finished its blow.

The **Mond** system is the outcome of an endeavour to recover the nitrogen contained in bituminous slack in the form of ammonia. At present, on account of the complication and expense involved, ammonia is not recovered in plants of less than 5,000 H.P. capacity. The Mond producer consists of two concentric wrought-iron shells, the inner one being lined for a portion of its height with firebricks. The top is arched, the bottom tapers towards the grate; the whole producer is held in position by brackets over a water-lute. The slack freshly introduced at the top is confined for a time in a bell-shaped casting, hung from the top of the producer, and surrounded by the hot gas. The vapours distilled off from the slack are forced to pass downwards through the hot zone, in which most of the tar is "fixed." By the time the fuel reaches the body of the producer it is free from volatile matter. The grate consists of fire-bars hooked into two cast-iron rings so as to form an inverted frustrum of a cone; the centre is entirely occupied by cinders, which reach to the bottom of the pit in which the producer stands, and are raked away below the water-level; these cinders support a large part of the weight of the fuel. The mixture of steam and air

used in the producer has to pass downwards between the two shells, entering between the fire-bars, and thus becomes highly heated. The hot gas from the producer passes through a regenerator, consisting of vertical double tubes of wrought-iron, in which it gives up much of its heat to the ingoing air and steam. The gas is next freed from tar and cooled to about 90° C. (194° F.) by spraying it with water in a chamber, and then passes up the acid tower, in which it meets a descending stream of ammonium sulphate solution containing 4 per cent. of free sulphuric acid, which retains the ammonia. The bulk of this solution is circulated continuously, a part being removed for evaporation when its strength amounts to about 37 per cent. of ammonium sulphate, and fresh acid added to the rest. From the acid tower the gas passes up another tower filled with wood-packing, down which streams cold water, which takes up a large proportion of the sensible heat of the gas. The hot water so obtained is made to warm and to saturate with moisture the air on its way to the regenerator described above.

The temperature in the producer must be kept as low as possible to prevent the ammonia being destroyed. This necessitates the injection of a large quantity of steam, which also helps to prevent caking. Where the ammonia is to be recovered, 1 lb. of bituminous fuel requires 2½ lbs. of steam and 3 lbs. of air; 1 lb. of steam can be obtained by regeneration: the other 1½ lbs. is obtained, if possible, from exhaust steam. About ½ lb. of steam is actually decomposed, and 4½ lbs. or 62 to 71 cubic feet of gas are obtained. The calorific value of the gas is about 140 B.T.U. or 35 Cal. per cubic foot. The gas contains about 80 per cent. of the potential energy of the coal used. Its average composition, without ammonia recovery, is CO, 11 per cent.; H, 27·5; CH_4, 2·0; CO_2, 16·5; and nitrogen, 43·0. In this case, 1 lb. of coal requires only 1 lb. of steam. Where ammonia is recovered—*i.e.*, when the temperature is kept lower and more steam used—the average composition of the gas is CO, 13·8 per cent.; H, 24·3; CH_4, 2·0; CO_2, 13·9; and nitrogen, 46·0.* It is claimed that about 70 per cent. of the nitrogen present, or about 90 lbs. of ammonium sulphate per ton of coal, can be recovered. Gas made in this way is especially suitable for large central stations supplying smaller consumers of power. But, in order to keep the mains within reasonable size, the gas must be delivered under fairly high pressure (10 lbs. per square inch); this necessitates the use of compressors, and of special means to guard against leaks in the mains. Mond gas appears to be a step towards the realisation of Sir Oliver Lodge and B. H. Thwaite's dream of

* Case, *J. Soc. Chem. Ind.*, 1905, p. 596.

smokeless cities deriving their power from producers situate at the pit's mouth.

Other means than that described above can be used for converting the sensible heat evolved in the formation of producer gas into chemical energy. Thus CO_2 may be substituted for water, its decomposition taking place according to the equation $CO_2 + C = 2CO$, which absorbs for every 12 kilos. of carbon thus gasified 39,000 Cal. The system is used for the preparation of a mixed gas corresponding thermally with semi-water gas, and consisting of a mixture of producer gas with addition of CO (instead of H + CO, as in the case of semi-water gas). Complete utilisation of the heat evolved in the formation of producer gas gives, on this plan, the ideal values—producer gas 65·3 per cent., CO (from CO_2) 34·7 per cent. Such an ideal gas would contain 57·1 per cent. CO and 42·9 per cent. N, and have a calorific value of 48 Cal. per cubic foot. As a supply of pure CO_2 is not available in most places without having recourse to special means of preparation,* this method is reduced in practice to the system of turning back a portion—*e.g.*, one-half—of the products of combustion of the furnace fed by the producer, into the producer itself. This CO_2 contained in these products of combustion is converted into CO, and the chemical energy (as distinct from the sensible heat) of the producer gas is thus increased. An advantage of this method is that the CO_2 to be decomposed is already heated, whereas in making semi-water gas an external source of heat is necessary for raising steam. In any ordinary method of working, the sensible heat of the products of combustion is, of course, largely recovered by the use of the regenerator. The disadvantage entailed is the dilution of the gas from the producer with the nitrogen of the products of combustion. At present this method is hardly used.

Blast-furnace gas is essentially a poor producer gas, containing much CO_2. Its composition is variable, but may be stated on an average as 25 to 30 per cent. of CO, and 15 to 20 per cent. of CO_2, the remainder being almost entirely nitrogen. The calorific value is about 23 Cal. or 90 B.T.U. per cubic foot. Blast-furnace gas is such a poor gas that it would not be used were it not a bye-product which must be obtained in any case. Only a portion of the total gas produced is needed to heat the air for the furnace blast, and the remainder is now utilised locally to a large and increasing extent for steam-raising and in gas engines. Before using it in the latter, the gas must be scrubbed free from the flue-dust it carries, and its dilution necessitates the use of

* An exception is found in the case of breweries. Lime-kiln gases are also fairly rich in CO_2.

large engines. For the same reason, it must be well mixed with air before burning it under a boiler.

Suction Plants.—All the gaseous fuels considered above are produced under a pressure somewhat above the atmospheric. When used in the gas engine, they are not delivered straight to the latter, but are first stored in a gasholder, from which they are delivered under slight pressure to the engine. Hence the type of plant has been distinguished as "*Pressure Gas-Producers.*" The constantly increasing use of gas engines has caused the evolution of gas producers along economic lines. During recent years a new type, requiring neither steam jet nor air blower has been evolved, the air being drawn into the producer by the sucking action of a gas engine. The expensive gasholder is entirely avoided; the producer is connected directly to the combustion chamber of the engine, the gas being merely cooled and passed through a scrubber containing coke or sawdust. This scrubber removes, not only tarry matter, but also drops of condensed moisture, which, with the usual magneto-ignition might cause short-circuiting, and so prevent ignition in the engine. In addition to a gasholder, the older type necessitated the use of a boiler to generate steam. With the suction type of plant the boiler is supplanted by an "evaporator" or "vaporiser," which in small plants is built frequently on the top of the producer in the form of a water-jacket, and in larger plants close to the producer as a tubular evaporator. This evaporator generates the steam required by utilising the waste heat of the producer and of the gas. This is of considerable advantage as compared with the old system, the firing of a separate boiler being dispensed with. The producer itself consists of an iron shell lined with firebrick, and provided with a suitable hopper. Before starting the engine the fuel in the producer is heated by means of a blower, which, in plants of less than 150 H.P. capacity, may be hand-worked. When the fuel is alight and the gas burns well at the test-cock the engine is started, and by its own sucking action draws the necessary air and steam into the producer as required for each stroke. From the producer the gas is drawn through the scrubber and an equalising tank to the engine. The gas-making process continues as long as the engine is moving, and stops when the engine stops. Either anthracite, charcoal, or coke can be used in suction-gas producers. The proper regulation of the supply of steam to air is a matter of some practical difficulty when the engine is not working at its full load. If too much steam is introduced, the temperature of the producer is lowered unduly. Some makers merely insert an opening through which the steam can escape; Dowson and

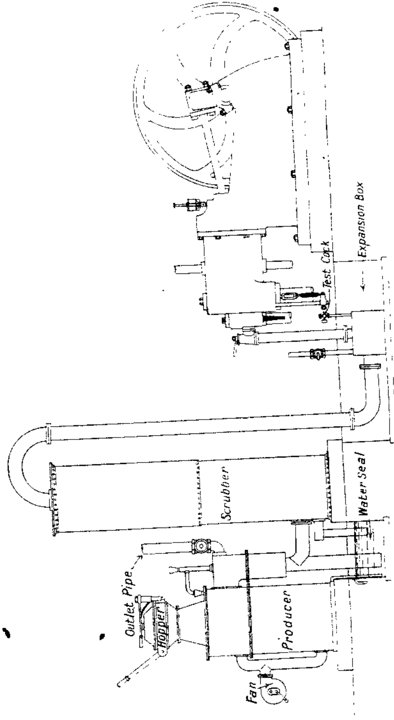


Fig. 10.—Smith's "suction gas plant."

others make the engine suck exactly the quantity of water needed during one stroke into a vaporiser, in which it is instantly and completely converted into steam. The gas made in a suction plant is similar to that made in an ordinary Dowson producer, but it contains a little more inert gas. The thermal efficiency of the gas is stated to be 80 to 90 per cent. of that of the coal used. When the engine is running under very light load, however, the gas produced is much poorer, and the full load should only be applied gradually, as the producer must be given a few minutes to recover its proper working temperature. Suction plant is advantageous where first cost and labour are to be kept down.

The utilisation of all the foregoing forms of generator gas may be effected in various ways, according as power, heat, or light is required. For mechanical power it may be burnt in a *gas engine*, the method being especially adapted for use where the demand for power is intermittent, as in electric light and power stations. In large works, generator gas (usually of the semi-water class) is made and stored and drawn upon to supply the gas engines as may be required; for small works, suction plants are used. In both cases, the stand-by losses are very much smaller than with steam engines. The method of using generator gas in a gas engine differs in no essential respect from that necessary for the employment of coal gas; the smaller volume of air for explosion, and the lower calorific value per cubic foot, being the only conditions of noticeable difference. The efficiency attained in a good gas engine burning semi-water gas is upwards of 25 per cent. With a heat efficiency of 80 per cent. in the gas used, the total efficiency becomes about 20 per cent., which compares favourably with the 10 to 15 per cent. efficiency of a steam engine. The use of generator gas for heating has been already mentioned under the description of the production of its various kinds. Its employment for lighting falls into two classes:—(1) Water gas is carburetted with the products of decomposition of petroleum * (see *Gas making*, Vol. II.); (2) generator gas, usually water gas, is burnt so as to heat a refractory material and to cause it to emit light. This principle is utilised in the *Welsbach light* (see Vol. II.), in which a "mantle" of refractory material is heated in a non-luminous gas flame (coal gas or water gas); the mantle is made by dipping a knitted cylinder of cotton thread, after it has been washed successively in ammonia and hydrochloric acid, into a solution containing, chiefly, nitrate of thorium, together with nitrate of cerium, and drying at 90° F. = 32° C. The oxides must be as pure as possible, as foreign matter, particularly iron, considerably diminishes

* This is now done on an enormous scale.

the illuminating effect. The gas must be thoroughly burnt lest carbon be deposited on the mantle and destroy it. The Fahnehjelm lighting system is similar in principle: rods of magnesia, set in a metal backing to form a comb, are heated in a water-gas flame and emit a full white light. The magnesia rods gradually shorten and wear away, and have eventually to be renewed. Methods of lighting of this class are economical of gas, a cheap non-illuminating gas, such as water gas, sufficing, and a larger percentage of the total energy of the gas being obtained as light by such means than by the direct burning of illuminating gas. The chief item of cost is the frequent renewal of the refractory material to be heated.

NATURAL GAS is a form of gaseous fuel confined to petroleum districts where it occurs associated with the crude oil. The following analyses * show its composition :—

	Per cent.	Per cent.	Per cent.
H, ...	35·9	20·6	Trace.
CH_4, ...	49·6	72·2	81·1
C_2H_6, ...	12·3	3·6	12·0
C_2H_4, ...	0·6	0·7	0·1
CO, ...	0·4	1·0	Trace.
CO_2, ...	0·4	0·8	0·1
O, ...	0·8	1·1	0·2
N, ...	..	..	6·5

The gas issues at great pressure from the earth (sometimes the pressure is as high as 70 atmospheres). The natural reservoir containing the gas under pressure is tapped (often when sinking a shaft for petroleum) in the manner described in the section on petroleum (*q.v.*), and is conducted by pipe lines to the place of consumption. It is burnt in the way usual for gaseous fuel, and is used for all kinds of manufacturing purposes, its freedom from sulphur giving it a special value for metallurgical purposes. On account of its poverty in heavy hydrocarbons, natural gas has a low illuminating value. The density of an average sample is 0·5 (air = 1), and its calorific value is about 222 Cal. per cubic foot. Besides its main use as fuel, natural gas has another employment—viz., the preparation of the pigment carbon black, which is made by the imperfect combustion of the gas and collection of the resulting soot (see *Pigments*, Vol. II.).

* The occurrence of helium, in quantities varying from a trace to nearly 2 per cent., in many samples of American natural gas is of scientific interest.

HYDROGEN has but a limited industrial use. Its chief employments are in producing high temperatures by means of the oxyhydrogen blowpipe—*e.g.*, in lead burning, iron welding, and platinum melting—and in filling military balloons. The most convenient method of preparing it consists in acting on zinc with dilute sulphuric acid. The hydrogen from scrap iron and an acid is always contaminated with hydrocarbons and sulphuretted hydrogen, which are generally reckoned objectionable. Cheaper, but less convenient methods, are—(1) heating a mixture of zinc and slaked lime, the reaction being

$$Zn + Ca(OH)_2 = ZnO + CaO + H_2;$$

(2) heating a mixture of anthracite and slaked lime according to the equation

$$C + 2Ca(OH)_2 = CaCO_3 + CaO + 2H_2;$$

(3) heating iron scrap in a current of steam, decomposition taking place as follows :—

$$Fe_3 + 4H_2O = Fe_3O_4 + 4H_2.$$

This last reaction can be utilised for obtaining hydrogen by reducing steam by means of semi-water gas, through the action of iron as an intermediary. Steam is first passed over heated iron (as scrap or bar), and hydrogen is produced according to the equation given above. The resulting ferroso-ferric oxide is then reduced by heating it in a current of semi-water gas, and the reduced iron again oxidised by steam, a further quantity of hydrogen being thus obtained. An extremely simple way of obtaining both hydrogen and oxygen consists in decomposing water (slightly acidified to render it conducting) by means of an electric current. The reason why this method has not hitherto been adopted, lies rather in the small demand for hydrogen (not warranting an expensive plant) than in the intrinsic cost of the process.* When both anode and cathode are of unattackable material—*e.g.*, platinum—O and H are both obtained, but by using an oxidisable material at the anode—*e.g.*, zinc—H alone may be prepared, and, in complementary manner, by using a reducible substance such as CuO at the cathode, the H may be suppressed and O alone liberated. Economy may be sometimes secured by such variation of method. The electrolysis of water is now carried out commercially for the preparation of the gases

* There might be a greater use of hydrogen if the gas could be supplied cheaply to small consumers. But the first cost of the steel cylinders in which the compressed gas is stored, and that of their transport, adds very largely to the cost of making the gas.

for oxyhydrogen blowpipe work (p. 41). The tank used is 6 feet long, 18 inches deep, and only 1½ inches wide. A vertical plate of iron is placed the whole length of the thin tank, so as to keep the gases apart as they are generated. This plate has a rectangular aperture, so as to permit the electrolyte to flow. The tank is closed by two rubber blocks between the centre plate and sides. The sides of the tank are of iron, and form the anode and cathode. To the water in the tank soda is added, and during electrolysis hydrogen is liberated at the cathode and oxygen at the anode. The gases are led off separately from the top, passing through a water-seal into gasholders. In each gas pipe a piece of platinum is kept red hot by an electric current, and this provision removes any traces of hydrogen from the oxygen and any oxygen from the hydrogen. Another process of theoretical and also practical interest is that devised by Mond for separating H from CO in water gas (*v.i.*).

OXYGEN.—This gas is substituted for air when it is required to produce the highest possible temperature by the combustion of a given fuel. The ease with which high temperatures may be obtained by means of oxygen is due to the absence of the diluting effect of the nitrogen with which the oxygen of the air is associated, such nitrogen having to be heated through the same range of temperature as the oxygen and the products of the oxidation of the fuel. Oxygen is especially used when hydrogen is the fuel adopted. It is almost invariably prepared from the air by taking advantage of some reversible reaction. The simplest reaction of this class used for preparing oxygen is that which occurs when barium oxide, BaO, is heated in air to form BaO_2, this product, when raised to a higher temperature, liberating oxygen and becoming reduced again to BaO. As originally carried out on a commercial scale by Brin, barium nitrate is heated in crucibles until its decomposition is complete, and a porous mass of BaO remains. This substance is heated in iron retorts to 600° C. = 1,112° F., and a stream of air, freed from CO_2 by scrubbing in a lime tower followed by one of caustic soda, led over it. Under these conditions BaO_2 is formed, and, on raising the temperature to 850° C. = 1,562° F., is decomposed giving off oxygen which can be collected and compressed into steel cylinders. According to more modern practice the retorts are maintained at a temperature of about 700° C. = 1,292° F., and the pressure varied. During the period when the pressure is about 10 lbs. above that of the atmosphere, oxygen is absorbed, and when the pressure is reduced to about $\frac{1}{15}$ of an atmosphere (absolute)—*i.e.*, a vacuum of about 28 inches—oxygen is given off, the process thus resolving itself into alternately pumping air

into the retorts, and exhausting oxygen from them. By this process only about 8 per cent. of the oxygen which a given weight of BaO is capable of absorbing in the formation of BaO_2 and subsequently giving up, is obtained in each operation; but the comparative rapidity of the alternate stages of the process, and the diminished wear and tear of the retorts, which are kept at a fairly constant temperature, more than compensate for this drawback. The oxygen always contains some nitrogen—*e.g.*, 5 per cent.—and thus is unsuitable for such purposes as require the highest temperature of the oxyhydrogen blowpipe. The process is now but little, if ever, used.

Another method of the same class consists in heating manganese dioxide with caustic soda in presence of air, whereby sodium manganate and steam are produced in accordance with the equation—

$$MnO_2 + 2NaOH + O = Na_2MnO_4 + H_2O.$$

The sodium manganate is then heated in a current of steam, and Mn_2O_3, caustic soda, and oxygen are produced, thus—

$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaOH + 3O.$$

When the oxygen has been collected, the mixture of Mn_2O_3 and NaOH may be again heated in air, and this last equation becomes reversed. Thus by heating a mixture of caustic soda and oxide of manganese in air and in steam alternately, a supply of oxygen can be obtained from the air.

A third reaction, greatly resembling the last, is that obtained by heating calcium carbonate and lead oxide in a stream of air (Kassner's process). The lead oxide is oxidised, calcium plumbate being produced according to the equation—

$$2CaCO_3 + PbO + O = 2CaO . PbO_2 + 2CO_2.$$

The resulting calcium plumbate is moistened and treated with furnace gases at a temperature below 100° C. = 212° F. The CO_2 of the furnace gases attacks the plumbate forming PbO_2 and $CaCO_3$. The mixture is then heated in a retort, whereby the lead peroxide is decomposed, and oxygen given off, its evolution being aided by injecting steam. On raising the temperature of the retort, the $CaCO_3$ is also decomposed, yielding CO_2 (which is used in the first stage of the process in the next cycle of operations), and a mixture of PbO and CaO is obtained, which on heating in air again yields $2CaO . PbO_2$, capable of undergoing the same series of changes.

Besides these purely chemical methods, a process based on the difference in solubility in water of oxygen and nitrogen—the

former being nearly twice as soluble as the latter—has been proposed for the commercial preparation of oxygen. By alternately compressing air over water, and then drawing off the dissolved gases from the water by creating a vacuum over its surface, a progressive enrichment in oxygen of the resulting mixture of gases takes place, until after eight absorptions and exhaustions a mixture containing 97·3 per cent. of O and 2·7 per cent. of N is produced.

Another method of separation not depending on definite chemical reactions is that which takes advantage of the property of an indiarubber membrane of allowing a readier passage of oxygen than of nitrogen, the process being known as dialysis. It is carried out by maintaining a vacuum inside a bag made of thin indiarubber, the air pumped out being found to be richer in oxygen than is atmospheric air. By repeating the process, approximately pure oxygen can be produced. The method in no way depends on the property of diffusion. The electrolytic preparation of oxygen may be effected simultaneously with that of hydrogen (*v.s.*). No practical outcome of these methods has *hitherto taken place.*

Probably the bulk of the oxygen used commercially (*e.g.*, for the synthetic manufacture of nitrates from air) is now made from **liquid air.** The liquefaction of air is accomplished by systematic cooling, advantage being taken of the fact that when *an imperfect gas, such as air, expands without doing external* work, its temperature falls owing to the internal work done. This cooling is known as the Joule-Thomson effect. The amount (d) of the cooling in degrees C. is given by the formula—

$$d = 0{\cdot}276\ (P_1 - P_2)\left(\frac{273}{T}\right)^2,$$

where P_1 is the initial, P_2 the final pressure of the air in atmospheres, and T its initial temperature in absolute degrees C. It is evident that the cooling effect is greater, the greater the reduction in pressure, and the lower the initial temperature of the gas. In carrying out the process according to **Linde,** compressed air is cooled by water, and allowed to expand through the outer of a pair of concentric tubular coils. In doing so, it cools a second quantity of compressed air, contained in the inner coil, to a temperature below its own initial temperature. The air first compressed expands into a chamber communicating with a pump, which again compresses it, and returns it to the inner coil, where it is cooled to a still lower temperature by the expansion of the second portion of air, which has in the meanwhile been transferred to the outer coil. The process is repeated

until liquid air is obtained. Of course, influx of heat from the outside must be prevented as far as possible.

The production of oxygen from liquid air is rendered possible by the fact that oxygen boils at a higher temperature, − 297° F. (− 183° C.) than nitrogen, − 321° F. (− 196° C.). Consequently, if liquid air is allowed to evaporate, the gas which is given off at first contains 93 per cent. of nitrogen, and only 7 per cent. of oxygen, the oxygen content of the liquid residue being proportionately increased. Thus, when about three-quarters of the total quantity has evaporated, the residue contains about 50 per cent. of oxygen. Much better yields of oxygen than this are obtained by systematically fractionating liquid air in vessels resembling the dephlegmators used for concentrating alcoholic liquids. In these vessels liquid air is made to boil at the bottom, the ascending vapours meeting slightly colder streams of liquid air, which trickle down baffle plates placed in the vessels. In so doing, the ascending vapours take up nitrogen from the descending liquid, the less volatile oxygen continuing its course downwards. A liquid rich in oxygen is thus obtained at the bottom of the vessel; this liquid is usually further treated in the same way in a second smaller vessel similar to the first. By this process it is possible to split up air into two portions, one as nearly pure oxygen, and the second nitrogen containing 7 per cent. of oxygen. This nitrogen is usually wasted, but occasionally finds an application in the manufacture of calcium cyanamide by leading nitrogen over heated calcium carbide. In this case, the impure nitrogen is further fractionated in a third vessel, the operation being conducted so as to yield a gas which is nearly pure nitrogen, and a liquid fairly rich in oxygen, which is returned to the first vessel. In many cases—*e.g.*, for furnace work—pure oxygen is not desired, and a gas enriched in oxygen up to 30 or 50 per cent. is made; such enriched air is often called "Linde-Luft."

SMOKE PREVENTION.—In connection with the loss of energy in furnace gases discussed on p. 83, attention must be drawn to the fact that the statement frequently made that the escape of much smoke means a large loss of fuel is erroneous. Even dense smoke represents less than 1 per cent. of the total fuel burnt. Bad economy is more often the concomitant of a smokeless chimney, which is frequently an indication of an excessive amount of air above that necessary for combustion, the wastefulness of which has been already pointed out. Smoke-prevention being necessary on other than economical grounds, attempts have been made to secure the suppression of smoke, or to remove it from the furnace gases after it has been formed.

The former aim is attained (*a*) by the use of non-bituminous fuel; (*b*) by careful stoking at frequent intervals (the destructive distillation of such portion of a heavy charge as does not immediately ignite being thus avoided); (*c*) by mechanical stokers, which effect the same end (*b*) still better; (*d*) by forced draught (often objectionable on account of the surplus air introduced); and (*e*) by a secondary air supply at a point beyond the main zone of combustion, the hot gases and fresh air being led over a fire-brick bridge or some similar device (*cf. Coalite*, p. 79). Smoke may be removed from furnace gases by washing with a water spray, and many modifications of this method have been devised. It is generally more economical to work a furnace somewhat smokily, and wash the products of combustion free from smoke, than to attempt to prevent the formation of smoke.

Frequent analysis of the flue-gases is necessary to control the economical working of a furnace. In the Orsat apparatus commonly used for this purpose, oxygen and carbon dioxide are determined, and, in addition, carbon monoxide, if the latter is present. After the best conditions have once been ascertained for any one kind of fuel, it suffices to know the amount of any one of the constituents of the flue-gases, in order to judge whether the furnace is working properly. Carbon dioxide is the gas most usually determined, and a number of instruments have been constructed to determine its amount more or less automatically and continuously. In the older instruments this was done by determining the specific gravity of the gases—*e.g.*, by leading the latter through a glass globe partly balanced by a second globe filled with air, and partly by weights. The method is not very reliable, since the specific gravity of the gases is dependent, not only on the quantity of carbon dioxide present, but also on that of the water vapour and on the temperature of the gases. Better results are obtained by instruments in which the quantity of carbon dioxide present is actually determined by absorption. The "Ados" or "Sarco" apparatus, and the Simmance-Abady "combustion recorder" work on this principle. In both the carbon dioxide is absorbed, by means of potassium hydroxide solution, at intervals of a few minutes, from fixed volumes of the gases, and the decrease in volume is registered automatically. In another form of apparatus the increase in weight of a vessel containing potassium hydroxide or soda-lime is continuously registered by a delicate spring-balance. In another instrument, termed "autolysator," the reduction in pressure of the gases after passing over soda-lime is determined, the gases in this case being forced to occupy a constant volume. To a third class belongs an instrument devised

by F. Haber, in which the refractive index of the gases is determined in a simple manner: a continuous record can be obtained photographically.

Useful information as to the working of the furnace is also obtained by a continuous determination of the temperature of the flue-gases (*cf.* p. 114).

Heating by Means of Electrical Energy.—Energy in the form of electricity is obtained from any prime mover, such as a steam engine, a gas engine, or a water turbine. It can be converted into heat by passage through a resistance which may be gaseous, as in an arc, or liquid as in a furnace of the type used in producing aluminium (*q.v.*), or solid as in a filament. Electrical furnaces used in chemical manufactures are usually of a mixed type, but instances can be cited of each. For the production of oxides of nitrogen by burning together the nitrogen and oxygen of the air a number of arcs are employed; for maintaining the temperature of a bath of electrolyte which must be kept fused the bath itself serves as a liquid resistance; for heating a mass of carbon and silica to obtain carborundum the resistance of the solids concerned, enhanced by their imperfect contact, is adopted. The fundamental condition in common is that there shall be a sufficient resistance at the point where the chemical reaction is to be induced.

The loss in converting the heat of combustion of ordinary fuel into electrical energy is so large that the application of the latter to commercial purposes is confined to special cases, but these include many of great industrial importance. It may happen that the reaction desired requires so high a temperature as to necessitate the use of a method independent of the temperature of dissociation of the oxides of carbon and of water. An example is furnished by the process of manufacture of carborundum already mentioned, or of graphite. The furnace used is of the resistance type, and is shown in the figure.

No mode of heating by the direct use of fuel is possible for this class of reaction.

Where lower temperatures are concerued, the choice between electrical and other methods of heating depends upon practical and economical considerations. The reduction of zinc from its oxide by heating with carbon requires a high temperature (1,100° C. = 2,012° F.), and can be reached by an ordinary furnace, but as the heat has to be applied at the outside of a retort containing the materials which are to be caused to interact, great loss occurs in transmission, and much damage to the retort takes place. These difficulties would be avoided by an electrical method of heating, which could be directed to the charge in the

retort instead of the outside of the vessel. In practice the advantage at present lies on the side of heating directly with fuel, but the inherent merits of internal heating are so large that an electrical method of reduction is possible if the source of electrical energy is sufficiently cheap.

Another example of electrical heating which is advantageous in spite of its relatively high cost is afforded by the aluminium furnace. Here the main purpose of the current is to deposit aluminium electrolytically, but as the electrolysis must be carried out in a fused electrolyte, it is found better to use a part of the current in fusing the electrolyte than to attain the same end by external heating with ordinary fuel. A figure showing a furnace of this class will be found in section on "Steel."

Heating jointly by an arc and by the resistance of the mass heated is employed in steel furnaces, such as the Héroult; simple resistance heating by a conductor of relatively small conductivity is exemplified by the Gin furnace.

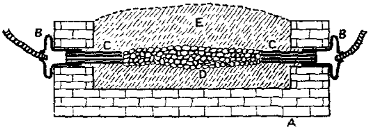


Fig. 11.

A, Brick box; B, heavy metal holders; C, carbon rods; D, core of broken coke; E, charge.

Obviously the resistance method may be applied to many sorts of industrial heating—*e.g.*, the roasting of ores, the baking of carbons, and even more domestic kinds of cooking—provided that the electrical energy is cheap enough or that the convenience attending its use outweighs its cost in money.

REFRIGERATION.—Great advances have been made in recent years in the production of practical and commercially successful machinery for mechanical refrigeration. In these machines there is a transference of heat from the substance to be refrigerated to the cooling agent, which is usually an evaporating liquid or an expanding gas. Certain practical considerations limit the choice of cooling agent. (1) It must be able to withstand reasonable changes of temperature and pressure. (2) Its capacity for heat should be large, in order that it may carry off the heat

extracted from the body to be cooled. (3) If the cooling agent is a liquid, its vaporising point must be low, it must evaporate rapidly, and the volume of the resulting vapour must not be too large. (4) *Its latent heat of evaporation must be as great as* possible. (5) Its vapour pressures at the temperatures employed must be practicable. Ordinary air is very abundant and admirably fulfils the first condition. Its capacity for heat, however, is small, and the machine must be correspondingly large. Moreover, a wide range of temperature is necessary, and experience shows that this means a comparatively low efficiency. Cold-air machines, therefore, are apt to be cumbersome and extravagant. Ether boils at 35·5° C., and at 0°C. has a vapour pressure of 18·4 cms., and a latent heat of evaporation of 94. At 0° C. therefore, it is necessary to evaporate 1,907 lbs. of ether to produce a ton of ice (to freeze 1 lb. of water at 0° C. requires the *abstraction of 80 lbs. °C. units of heat). Alcohol has a higher* specific heat than ether, but is less volatile. Opinions differ as to the most suitable cooling agent, but the three most commonly employed are carbon dioxide, ammonia, and sulphur dioxide. Carbon dioxide is cheap, and needs comparatively small compression plant. At ordinary temperatures it is liquefied by a pressure of 850 lbs. per square inch. Ammonia has the advantage that it is liquefied at a lower pressure—120 lbs.—but it requires a larger compression plant. Liquid ammonia boils at − 35° C., and has a vapour pressure of 318 cm. at 0° C. (*i.e.*, more than four atmospheres); it is, therefore, volatilised very rapidly at 0° C. Moreover, its latent heat of evaporation is as much as 294, so that the evaporation of a minimum of 610 lbs. liquid ammonia is theoretically sufficient for the production of a ton of ice. One great drawback to the use of ammonia is that in the presence of air it will dissolve copper, so that in ammonia machines the use of this metal or its alloys must be avoided in any parts which come in contact with the ammonia. Ammonia machines are, therefore, unsuitable where only sea water is available for cooling, as the iron pipes which alone can be used are quickly corroded by sea water. Liquid sulphur dioxide boils at − 11° C., has a vapour pressure of 116·5 cm. (1½ atmospheres) at 0° C., and a latent heat of evaporation of 95. It is, therefore, a volatile liquid presenting considerable advantages, but it is somewhat corrosive, since it is liable to be converted, by oxidation, to sulphuric acid. Modern refrigerating machines may be classified broadly thus—(1) Those in which air is used as the working substance; (2) those in which some liquid is alternately vaporised and liquefied during a cycle of operations. In the latter class of machine we may restore the vapour to the liquid state by (*a*)

mechanical compression, or (*b*) absorption, in which the solution of the vapour by some other substance acts as a substitute for mechanical compression. In all these various systems the same general principle is involved. When a gas is compressed its temperature rises. The converse of this is also the case. When a gas expands, it does work and loses an equivalent amount of energy in the form of heat. The heat developed by the compression of the gas (which may involve its liquefaction) is removed by a current of cold water. The condensed and cooled gas is then allowed to expand in suitable vessels, and the refrigerating effect thus produced is utilised in some convenient way (see also *Liquid Air*, p. 99).

Cold-air Machines.—A steam engine is generally employed as the motive power for compressing the air in the compression cylinder from atmospheric pressure, and a temperature of about 20° F. to a pressure of about 65 lbs. per square inch and a temperature of 270° F. The compressed air is then delivered to a cooler, where its temperature is reduced to about 70° F., and a considerable amount of its moisture removed as condensed water by circulation through water-cooled metal tubes. The air may then be circulated through a drier, in which a further quantity of moisture is removed either by simple cooling in tubes or by centrifugal action. The air now passes to the expansion cylinder, the temperature of exhaust being about − 80° F. The moisture corresponding to the difference in humidity between the temperatures of inlet and outlet is deposited as snow in snow boxes, and is regularly removed. The cold air is now utilised for cooling chambers or some similar purpose, and finally returned to the compressor.

Vapour Compression Machines.—By means of a compressor, an easily liquefiable gas, such as CO_2, NH_3, or SO_2, is condensed to a liquid in a condenser consisting of a long coil of tubing surrounded by water, which absorbs the heat given out by the gas as it liquefies, the warm water passing away and being constantly replaced by fresh, cold water. The liquefied gas now passes through a regulating valve to the evaporator, in which it is rapidly converted into gas. In doing this it absorbs heat from the brine surrounding it, so that the latter is cooled to a low temperature. The gas leaves the evaporator, passes again to the compressor, and the cycle of operations is repeated. In a common form of carbon dioxide refrigerating machine which can be used for cooling brine for cold storage chambers, for making ice and for various other purposes, the condenser coils are contained in an annular vessel surrounding the evaporator, a space fitted with an insulating material being left between the

two. The crank shaft not only works the compressor, but also a small pump which drives the cooled brine from the inner vessel, and causes it to circulate through the pipes in the cold storage rooms. These brine tubes are known as "grids," are made in long lengths electrically welded, and are generally placed at the top of each storage chamber under the ceiling. A 25 per cent. solution of calcium chloride is commonly employed as "brine," and is preferred to a solution of common salt, since it does not freeze so readily. Such a solution has a specific gravity of 1·22, specific heat 0·70, and freezes at a temperature of − 18° F. A solution of magnesium chloride is also sometimes used for this purpose, a 25 per cent. solution having a freezing point of − 22° F. and a specific heat of 0·70.

Absorption Refrigerating Machines.—In these machines a liquid evaporates under conditions which can be readily maintained, and the resulting vapour is absorbed by another liquid. In one of the earliest of these processes—due to Edmund Carré—water was used as the evaporating liquid and sulphuric acid as the absorbent. Ferdinand Carré invented the "ammonia absorption machine," which has been improved by various inventors until at the present time it is regarded as an important type. Its action is due to (1) the affinity of water for ammonia gas, (2) vaporisation of ammonia from its aqueous solution and subsequent condensation to liquid ammonia, and (3) vaporisation of liquid ammonia, which produces the refrigerating effect, the gas being again absorbed by water. The following brief description of the plant used may be of interest:—

Strong ammonia solution (sp. gr., ·880) contained in a "**generator**" is heated by steam coils carrying steam at 60 to 75 lbs. pressure. Ammonia gas and water vapour are thus driven off, and pass into the "**analyser,**" in which the bulk of the water is retained by means of baffle plates, the temperature of which is kept at about 180° F. by circulation of the ammonia liquor feed on its way to the generator. The gas then passes through a "**rectifier,**" which reduces its temperature still further, and condenses more water, which drains back to the generator. The almost anhydrous ammonia gas is then liquefied in a "**condenser,**" after which it passes through a regulating valve, which reduces its pressure from about 160 to 35 lbs. per square inch, into some form of "**cooler,**" where it evaporates and produces the desired refrigerating effect. From the cooler the gas passes through another regulating valve into the "**absorber,**" where it is absorbed by weak liquor (from the "generator"), which trickles over water-cooled pipes in an atmosphere of the gas. The strong liquor so produced, at a temperature of about 120° F., is finally

sent back to the "generator," passing *en route* through the "**exchanger**" and "**analyzer.**" In the former the weak liquor, at about 270° F., on its way to the absorber, separated, of course, by coils, meets the strong liquor at a lower temperature—about 120° F.—on its way to the "generator," an economical interchange of heat being the result, the temperature of the strong liquor being raised to about 180° F., and that of the weak liquor reduced to about 210° F.

The applications of refrigeration are very numerous, the most important being for the transportation and storage of perishable merchandise both by land and sea. It is also extensively applied in cooling in breweries, when the temperature of the "wort" has to be kept within certain defined limits, so as to allow the fermentation to take place under the proper conditions.

MEASUREMENT OF TEMPERATURE.—The fact that two quantities of fuel yield the same quantity of energy on combustion, does not imply that the energy they yield is of the same intensity—that is, that the heat produced is at the same temperature. It is obvious that the larger the quantity of heat evolved by the combustion of a given weight of fuel and the smaller the weight of the products of combustion and ash, the higher will be the temperature of the burning mass and of its products and ash. When the weight and the specific heat * of the products of combustion are known, it is possible to calculate the maximum temperature (the "calorific intensity") which could be produced by the combustion of the fuel, when no limiting factor is active. In the case of fuel burning in oxygen free from a diluting gas—*e.g.*, nitrogen—the calculated temperature is considerably higher than that of the dissociation of the chief products of combustion, CO_2 and H_2O; when nitrogen is present (as when air is used) the diluting effect of the inert gas is sufficiently great to lower the calculated temperature to about the dissociation temperature. It is probable that at industrial high temperatures a portion of the gaseous products of combustion is, for a period at least, in a state of dissociation. Owing to the facts that the specific heats at high temperatures of the products of combustion of fuel are not accurately known, that the amount of dissociation is also uncertain, and that loss by conduction and radiation greatly increase with rise of temperature, the calculation of the maximum temperature that shall be produced by a given fuel is futile. Direct measurement is therefore necessary.

* This being, of course, taken at the temperatures concerned, at which it is considerably higher than at ordinary temperatures.

METHODS FOR MEASURING TEMPERATURE may be classified as follows :—

1. Measurement of alteration in volume of bodies.
2. Observation of change of state of substances.
3. Measurement of alteration in electrical resistance.
4. *Measurement of the E.M.F. of a thermo-electric couple.*
5. Measurement by optical methods.
6. Calorimetric measurement.

1. Taking these in order, the first is the method most frequently used, and is that exemplified by the common thermometer, a description of which is here unnecessary. An ordinary thermometer, filled with mercury and having only mercury vapour in the space above the mercury column, is fairly reliable up to 300° C. = 572° F.; but if higher temperatures are required, the space above the column must be filled with some inert gas, the pressure of which will raise the boiling point of the mercury. Thus, nitrogen-filled thermometers may be used up to about 400° C. = 752° F., and thermometers containing CO_2 at a pressure of 20 atmospheres to 550° C. = 1,022° F. An alloy of sodium *and potassium, liquid at the ordinary temperature*, has also been used, on account of its high boiling point, for thermometers up to about 500° C. = 932° F. The accuracy of a thermometer is much influenced by the character of the glass used in its construction. Ordinary glass contracts slowly after having been blown into bulb form, thus causing a rise in the reading of the thermometer. Preparation of the bulb years before use decreases this defect. Special glass, prepared at Jena, for which freedom from this tendency is claimed, has one of the following compositions :—

	I.	II.	III.
SiO_2,	67·5	52·0	69·0
Al_2O_3,	2·5	..	1·0
CaO,	7·0	..	7·0
ZnO,	7·0	30·0	7·0
Na_2O,	14·0	..	14·0
K_2O,	..	9·0	..
B_2O_3,	2·0	9·0	2·0

Alcohol thermometers are made for low temperatures, but the dilatation of alcohol is by no means as regular as that of mercury.

The methods of measuring temperature which depend upon the expansion of solids by heat have but little application, as

expansion of most solids is small and irregular, needing multiplication and correction before it can be utilised for measuring temperature. Moreover, when used at high temperatures, most solids are apt to take a permanent set, impairing subsequent observations, unless they are frequently recalibrated. An alteration of volume by rise of temperature—not due to separation of molecules, but arising from increase of aggregation by incipient sintering, and amounting, therefore, to a contraction instead of an expansion—has been used in the clay industries for roughly estimating the temperature of kilns. The method, which consists in observing the shrinkage of a test piece of plastic clay (see *Clay Industries*, Vol. II.), was originated by Wedgwood; the clay test piece is measured, after exposure in the furnace, by dropping it into a wedge-shaped groove.

Since the expansion of gases, the critical temperatures of which are much below the ordinary temperature of the air, is for ordinary high temperatures approximately regular for a given increment of temperature (viz., $\frac{1}{273}$ of the volume of the gas at 0° C. for each degree C.), such gases (*e.g.*, air and hydrogen) may be employed for measuring temperatures by their expansion. The apparatus necessary consists essentially of a bulb of glass, porcelain, or platinum, of known volume, which is attached to a capillary tube, serving to make connection with the measuring part of the apparatus. This bulb is inserted into the space the temperature of which is to be measured, the capillary tube protruding for observation. The known volume of gas in a gas thermometer may be allowed to vary, and its increase of volume be measured at constant pressure, or, conversely, the volume may be kept constant and the pressure requisite for this may be measured. Certain objections arise to either of these plans singly. Thus, in the first case, when the gas is allowed to expand under constant pressure, a portion of it is expelled from the bulb into the measuring part of the apparatus (consisting essentially of an index of liquid in a graduated tube); this portion is no longer subjected to the temperature to be measured, so that as the temperature rises, a continually decreasing quantity of gas is being caused to expand in the bulb of the thermometer, necessitating a correction; consequently the delicacy of the instrument decreases with rise of temperature (since the fraction $\frac{1}{273}$ is referred to the volume at 0° C.). In the second case, where the volume of the gas is kept constant, this objection does not arise, but on the other hand, a moderate rise of temperature—*e.g.*, from 0° to 273° C. = 32° to 523° F.—means a large increase of pressure on the bulb, such as one atmosphere in the case quoted. The considerable pressure thus caused at

high temperatures becomes serious when the material of the bulb reaches its point of plasticity. To overcome these objections a pyrometer has been devised by Wiborgh (*Journ. Soc. Chem. Ind.*, 1889, 214), the principle of which is as follows:—A porcelain bulb, connected by a capillary tube to a manometer, is exposed to the temperature to be measured. The gas within it *is allowed to expand and escape until the temperature of the* bulb has reached that of the furnace in which the apparatus is used. A measured volume of gas, representing a known fraction of the volume of the gas in the pyrometer bulb, and being at a known temperature lower than that of the bulb (*e.g.*, the temperature of the outer air), is then forced into the heated bulb, and the expansion consequent on the rise of temperature of this air is measured by the pressure required to balance it: this pressure is obtained by raising the mercury in the manometer tube, and gives the necessary data for calculating the temperature of the main bulb of the apparatus. The following expression will represent the application of the data:—

$$V = H \frac{V + V_1 \left(\frac{T - 273}{t - 273} \right)}{H + h}$$

T is the temperature to be measured, t that of the portion of air forced into the bulb, V the volume of the bulb, V_1 the volume of the air forced in, H the pressure of the atmosphere at the time of observation, and h the pressure required to balance that of the air which has been forced in, after it has expanded.

The apparatus necessary is represented diagrammatically by the accompanying figure, in which V is the bulb of the instrument, B the manometer tube, $m_1 - m$ the volume of gas driven in, and h the height of the column of mercury in the manometer balancing the increase of pressure. K is a collapsible rubber ball serving to inject the gas and to adjust the manometer level.

By such an arrangement the objections that are valid against the two types of gas pyrometers described above are avoided. For although during the measurement the volume of heated gas is kept constant, the increment of pressure to be measured is not large, depending, as it does, on the volume of the small quantity of air introduced before each measurement.

Gas thermometers are available through a large range of temperature, serving both as low temperature thermometers and as **pyrometers,** a term applied to thermometers for measuring high temperatures. An alternative method of applying the expansion of a gas for the determination of temperature, which requires no special apparatus, consists in heating a refractory

vessel of known volume, containing hydrogen, air, or iodine to the temperature to be measured, sealing the exit end of the vessel, and ascertaining the quantity of gas remaining in the vessel: this determination may be effected either by direct weighing of the sealed globe; or, for air and hydrogen, volumetrically by sweeping it out with a current of hydrogen chloride and measuring it over water (in which hydrogen chloride is soluble); or gravimetrically for hydrogen by oxidation and weighing as water. The use of iodine presents the advantage that its vapour is heavy; but as it dissociates above 1,000° C. = 1,832° F. it cannot be used at high temperatures.

In yet another method, which can be made continuous in operation and capable of indicating results at a distance from the furnace, air, heated to the temperature to be measured, is passed through a small orifice, cooled to a known temperature, and then passed through another small orifice of the same dimensions as the first. The volume of the air passing both orifices is the same at the orifices, but within the intermediate space it undergoes a contraction registered by an alteration of the pressure which the air exerts. This pressure is indicated on a manometer, if necessary at a distance. This method is not used now.

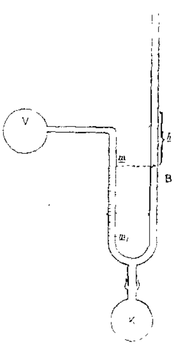


Fig. 12.
Wiborgh's Pyrometer.
V, *Bulb*; B, manometer; $m_1 - m$, volume of injected gas; *h*, height of mercury; K, rubber ball.

It should be said that temperature measurement by the gas thermometer is still the fundamental method. It is too cumbersome, however, for technical work; and since it has been shown that both the resistance and thermo-couple methods (*v.i.*) give results almost identical with those of the gas thermometer, these methods have been widely used, and have served, in their turn, to standardise the more recent optical methods.

2. This method depends upon the fact that the change of state of a pure substance occurs at a constant temperature when the pressure is constant. It usually consists in observing the behaviour of substances of known melting point or boiling point, when a test piece of the substance is exposed to the temperature

to be measured. An example of the method is given in the section on *Clay Industries*, Vol. II., under the head of *Seger's Normal Cones*. Alloys of silver, gold, and platinum of known melting point are also sometimes used. "*Sentinel pyrometers*," mixtures of alkali salts of definite melting points, have been applied in the thermal treatment of steel.

The following figures constitute a fair range of temperatures which can be determined in this way:—

		Cent.	Fahr.
Lead,	m.p.,	325° =	617°
Mercury,	b.p.,	358° =	676°
Zinc,	m.p.,	419° =	786°
Sulphur,	b.p.,	444° =	831°
Boric anhydride,	m.p.,	577° =	1,071°
Potassium iodide,	m.p.,	634° =	1,173°
" bromide,	m.p.,	699° =	1,290°
" chloride,	m.p.,	734° =	1,353°
Sodium chloride,	m.p.,	800° =	1,472
" sulphate,	m.p.,	883° =	1,621°
Zinc,	b.p. (circ.),	934° =	1,713°
Silver,	m.p.,	960° =	1,760°
Gold,	m.p.,	1,062° =	1,944°
Potassium sulphate,	m.p.,	1,070° =	1,958°
Copper,	m.p.,	1,083° =	1,981°
Palladium,	m.p.,	1,535° =	2,795°
Platinum,	m.p.,	1,710° =	3,110
Iridium,	m.p.,	2,203° =	3,997°*
Tantalum,	m.p.,	2,250° =	4,082°
Carbon,	m.p. (circ.),	3,500° =	6,332

3. The electrical resistance of a pure metal increases with the temperature, a fact which has been utilised for the determination of temperatures by measuring the resistance of a platinum wire exposed to the temperature to be ascertained. The modern form of the instrument is due to Callendar and Griffiths. It is shown in diagram in Fig. 13, and consists essentially of a fine platinum wire, P, wound on a mica frame, and enclosed in a doubly-glazed porcelain or in a quartz tube. This fine platinum wire is connected to two stouter wires, which terminate in screws at the base of the actual pyrometer tube, where they are joined to ordinary copper leads. In order to allow for the varying resistance of the leads, two platinum wires, L, exactly similar to the first two, but directly connected together, are placed in the pyrometer tube, and joined at its end to two copper leads similar to the other pair. The four copper leads are connected to a resistance box of the usual pattern. In the diagram, C indicates the Weston cadmium cell generally used to give a constant current, G the galvanometer, B the bridge itself with its sliding

* According to Nernst; Rasch gives 2,285° C. = 4,145° F.

contact, R_1 and R_2 two equal resistances in two arms of the circuit, and R_3 another resistance partly balancing that of the fine wire P *in the third arm. The resistance of the fine platinum* wire is usually determined at two known temperatures—*e.g.*, 0° and 100° C. (32° and 212° F.) and at the unknown temperature. As the variation in the resistance over a known range is thus determined, and the resistance of platinum varies according to a known formula, the unknown temperature can be computed.

4. When a junction of two dissimilar metals is heated to a temperature above that of their remote ends, an electrical current is generated in any circuit connecting them, the E.M.F. of which is proportional to the difference of temperature between the heated junction and the portions of the metal pieces which are kept cool. The measurement of the E.M.F. will, therefore, serve as a measurement of this difference of temperature. This principle has long been used in the case of the *thermopile*, which consists of several such thermo-electric couples arranged so that one set of junctions to be heated may be exposed to the source of heat the temperature of which is to be measured, the other set being allowed to remain cold, or intentionally kept so. The older forms of thermopile were made of metals giving an E.M.F. relatively considerable—*e.g.*, bismuth and antimony. The fusibility *of these substances prevented their application to the* measurement of high temperatures. For pyrometric work, a couple consisting of platinum and an alloy of platinum with 10 per cent. of rhodium or 10 per cent. of iridium is used. The former can be used up to 1,600° C. (2,912° F.), whereas the latter is accurate only up to about 1,400° C. (2,552° F.), but it has the advantage of giving a higher E.M.F. than the first, and is very widely used. Besides these, a copper-constantan * couple with a high E.M.F. is used for temperatures up to 500° C. (932° F.), and iron-carbon or nickel-carbon are occasionally used (for the sake of cheapness) at intermediate temperatures. The couple is

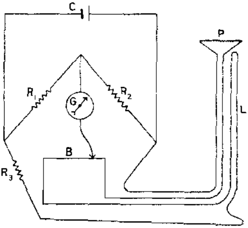


Fig. 13.

* Constantan is an alloy containing 60 per cent. of copper and 40 of nickel. It is used for resistance wire as well as for thermo-couples.

8

exposed to the temperature to be measured and the current generated is passed through a high resistance reflecting galvanometer, the deflections of which are proportional to the E.M.F. of the current (on account of the high resistance of the circuit), and, therefore, vary with the temperature to which the couple is exposed. The instrument is calibrated by immersing the junction in substances of known fusing point. Both resistance and thermo-couple pyrometers lend themselves to continuous recording of temperature. This was formerly effected photographically, but is done mechanically in all modern instruments. For this purpose, the galvanometer needle is depressed at fixed intervals of time against a cylinder of squared paper revolved by clockwork; by the aid of an inked ribbon or thread a fixed point on the needle makes a mark on the paper, which indicates the temperature.

Electrical pyrometers are used for such purposes as the determination of the temperature of the hot blast from Cowper's stove (see *Iron*), annealing furnaces, flue-gases, cold-storage rooms, etc.

5. Optical methods of measuring temperatures are finding increasing application to furnace work. A rough estimation of temperature by the eye has long been in use in the arts, but the estimated values were much too high. In the following table, the usual technical names and the corresponding measured temperatures are given :—

	Cent.		*Fahr.*
Just visible redness,	475° C.	=	878° F.
Dull red,	550-625°	=	1,022-1,157°
Cherry red,	700°	=	1,292°
Bright red,	850°	=	1,562°
Orange,	900-1,000°	=	1,652-1,832°
Light yellow,	1,050°	=	1,922°
White,	1,150°	=	2,102°

This method of judging temperatures is too subjective to be of much value.

Le Chatelier was the first to attempt the measurement of the light emitted by incandescent bodies photometrically, and more recently several instruments have been constructed which measure high temperatures with an error of only about 10° C. = 18° F. or less. They all depend on the Stephen-Bolzmann law, according to which

$$E = K\,(T^4 - T_0^4);$$

where E is the total energy radiated by a body at absolute temperature T to surroundings at absolute temperature T_0, and K is a constant depending on the units used. This law is true

only for the light radiated by a perfectly black body, bright bodies radiating less light. It has been shown, however, that hollow furnace chambers of even temperature, even when filled with flame, behave as black bodies, provided that the observation hole is small compared with the distance to the nearest solid body behind it. Moreover, in many industrial cases, only comparative measurements are desired, and in such cases what is known as the "black-body temperature"—*i.e.*, the temperature of a bright body indicated optically—although considerably below the *real* temperature of the bright body, will give accurate *comparative* indications. The distance of the instrument from the hot body or furnace aperture is of less importance than might at first sight be supposed. In practice the image of the hot body is never focussed to a point: hence, as long as the image formed is sufficiently large to overlap the spot viewed or the point of the thermo-couple (*v.i.*), its actual size and consequently the distance from the hot body is of no importance. To secure this, the size of the hot body should bear a certain minimum relation (stated with each instrument) to the distance of the pyrometer from it.

As regards the actual instrument used, in **Wanner's** pyrometer the light from the hot body is polarised, and that part of the light corresponding to Fraunhofer's line C (red light) is compared with similar light obtained from a small electric incandescent lamp. To avoid errors due to changes in the carbon filament of the latter, it is compared, from time to time, with the light emitted from a standard amyl acetate lamp. In the **Féry radiation** pyrometer, an image of the hot body is focussed on to the end of a copper-constantan thermo-couple, which is connected with a galvanometer. This form of instrument is often used with a recording arrangement (*v.s.*). The **Féry absorption** pyrometer is a less accurate instrument, in which the light from the hot body is brought to the same degree of intensity as light from a standard lamp by interposing a pair of wedges of absorbing glass to a greater or less extent. The first two pyrometers, on account of their freedom from breakage and comparative accuracy, are widely used; the third form is occasionally useful for measuring the temperature of small but intensely hot bodies—*e.g.*, electric light filaments. For measuring temperatures above 2,000° C., all three instruments are provided with reducing diaphragms, or standard absorbents.

6. A method differing essentially from any of the foregoing is the calorimetric method, in which a given weight of a substance of known specific heat is raised in temperature to that to be measured, and then cooled by immersion in a known weight of

water, the rise of temperature of which is ascertained. The most suitable substance for this purpose is platinum, the specific heat of which is known with fair accuracy between 0° C. and 1,200° C. = 32° and 2,192° F., being 0·03350 at the former temperature and 0·03818 at the latter. This method is naturally discontinuous unless several apparatus be employed in succession.

A modification consists in the use of a stream of water of known temperature circulating through a copper tube coiled in the space the temperature of which is to be determined. By a knowledge of the quantity of water flowing, of the difference of its temperature at influx and efflux, and of the specific heat of water, the number of calories imparted through the copper tube can be ascertained. This can be translated into temperature after the indications of the instrument have been standardised by observing its readings in a furnace, the temperature of which is gauged by its ability to fuse substances of known melting point. A variation of this method, especially applicable to hot blast stoves, consists in diluting the hot blast with a known proportion of cool air of known temperature and reading the temperature of the mixture.

Wiborgh's thermophones do not belong to any of the above classes. They consist of small cylinders of fireclay or graphite filled with an explosive mixture, and explode with a sharp report when thrown into a furnace, at the end of an interval of time corresponding with the temperature.

Since modern methods of pyrometry, especially the use of the thermo-electric apparatus, have been available, it has been found that most industrial temperatures are lower than was formerly supposed. The following are given on the authority of Le Chatelier * :—

	Cent.		Fahr.
Melting point of grey cast iron, . . .	1,220°	=	2,228°
,, ,, ingot iron (C = 0·1 per cent.),	1,475°	=	2,687°
,, ,, hard steel (C = 0·9 per cent.),	1,410°	=	2,570°
Bessemer converter (at finish), . . .	1,580°	=	2,876°
Open hearth steel furnace (at tapping), . .	1,580°	=	2,876°
Crucible steel furnace, ...	1,600°	=	2,912°
Puddling (temperature of bloom), . . .	1,330°	=	2,426°
Blast furnace (*in front of twyer*), . . .	1,930°	=	3,506°
Crucible glass furnace, ...	1,375°	=	2,507°
Siemens' tank glass furnace, ...	1,400°	=	2,552°
Hard porcelain furnace, ...	1,370°	=	2,498°
Incandescent carbon lamp filament, .	1,800° to 2,100°	=	3,270° to 3,812°

* These figures, which were obtained in 1892, are retained here chiefly for their historical interest. They have been well confirmed, on the whole, by more recent measurements.

DIRECT CONVERSION OF CHEMICAL ENERGY INTO ELECTRICAL ENERGY.—Certain chemical reactions, capable of causing evolution of heat, can be made to take place under such conditions that a portion of the heat appears as electrical energy. Thus, when 65 grams of zinc are dissolved in dilute sulphuric acid under ordinary conditions 37 Cal. are evolved, and no current which can be utilised is generated. When, however, zinc is allowed to dissolve in a cell containing a piece of platinum,* and is connected with this platinum by an external wire, a smaller quantity of heat is evolved in the cell, and the balance of the energy represented by the 37 Cal. due to the dissolution of the zinc appears as electrical energy in the wire. That fraction of the chemical energy liberated by the dissolution of the zinc which appears as electrical energy varies according to the nature of the substance used as the opposing electrode. When this substance is chemically inert, as are platinum and carbon for instance, the fraction of energy converted into electrical energy is large, the reverse being true when the substance forming the opposing electrode is comparatively active—*e.g.*, copper. Since the action of a simple cell causes a film of hydrogen to be deposited on the plate opposing the zinc, this plate becomes, to all intents and purposes, equivalent to one of hydrogen, a substance less inert than the subjacent material. The fraction of chemical energy converted into electrical energy by a cell having a plate thus "polarised" by a film of hydrogen is smaller than that proper to the couple originally composing the cell. Mechanical devices, such as roughening the platinum, and thus preventing the attachment of hydrogen, are moderately effective in mitigating this drawback.

A given quantity of zinc, dissolving under such conditions that it generates a current of electricity, always produces the same quantity of electricity, but the pressure at which this quantity is delivered varies according to the nature of the electrode opposing the zinc, an unattackable electrode giving a higher electrical pressure (E.M.F.) than one susceptible of attack. It must be remembered that electrical energy is the product of a quantity of electricity into electrical pressure (quantity $\times$ E.M.F.). Whence it follows that as the quantity is constant for the dissolution of a given weight of zinc, the corresponding amount of electrical energy produced varies directly with the E.M.F. of the couple (zinc and the opposing electrode).

The dissolution of zinc in dilute sulphuric consists, in effect,

* Which should be platinised to facilitate, by the roughness of the surface, the escape of hydrogen due to the dissolution of the zinc.

in the oxidation of zinc accompanied by the reduction of water with liberation of hydrogen. For simplicity's sake, the small energy changes due to the subsequent formation of zinc sulphate need not be considered here. The energy available for conversion into electrical energy in a simple cell, in which zinc is thus dissolved, is, therefore, measured by the difference between the heat of formation of ZnO and of H_2O * (85·8 – 68·4 = 17·4 Cal.). It is plain that if the hydrogen can be prevented from escaping free from an electrical cell, but, on the contrary, is burnt in the cell, the minus quantity in the above equation is reduced or eliminated. This condition is secured by the use of compound cells, in which the hydrogen that would otherwise appear at the electrode opposed to the zinc is suppressed thereat by a suitable oxidant. Such a suppression of hydrogen not only yields a larger fraction of the chemical energy as electrical energy, but obviates the necessity for preventing polarisation of the electrode opposing the zinc by means of mechanical roughening of the plate, for depolarisation is effected *pari passu* with the suppression of the hydrogen.

The **Daniell cell** is a typical compound cell. It consists of zinc in zinc sulphate or dilute sulphuric acid, and copper in copper sulphate, the two liquids being separated by a porous pot. The fundamental chemical changes consist in the dissolution of zinc in the form of sulphate in one compartment, and the deposition of copper from the sulphate, in the metallic state in the other compartment; the balance of chemical energy capable of conversion into electrical energy is represented by the difference between the heats of formation of $ZnSO_4$ and $CuSO_4$,* in solution—that is, 248·5 – 198·4 = 50·1 Cal. In this case the hydrogen is suppressed by the action of the copper sulphate in the copper compartment of the cell, and its equivalent of copper is precipitated upon the copper electrode; the whole of the energy represented by the hydrogen is, therefore, not utilised, as copper is reduced in its place. For a cell thus working, with elimination of copper instead of hydrogen, the Daniell cell is remarkably efficient, inasmuch as the quantity of electricity corresponding with the dissolution of a given weight of zinc is delivered by this cell at the maximum possible E.M.F.

Since the chemical energy of a Daniell cell is equivalent to 50·1 Cal. for the dissolution of 65 grams of zinc, and since 1 unit of electrical energy (1 unit of quantity × 1 unit of pressure) is equal to 0·241 gram unit of heat, the electrical energy

* Molecular quantities, expressed in grams.

corresponding with the chemical energy of a Daniell cell is

$$\frac{50 \cdot 1 \times 1000}{0 \cdot 241} = 207{,}900 \text{ (nearly) electrical units of energy.}$$

Seeing that 1 gram equivalent (32·5 grams) of zinc, in accordance with Faraday's law, corresponds with 96,540 units of electrical quantity (coulombs), the E.M.F. at which this electrical quantity must be delivered in order to be equal to the total electrical energy is

$$\frac{207{,}900}{96{,}540 \times 2} = 1 \cdot 07 \text{ units of electrical pressure, that is, volts.}$$

Other forms of compound cells are used in which zinc is the metal attacked, and thus employed as a source of energy, whilst *the opposing electrode may be composed of various materials*, and be immersed in several distinct **depolarisers.** Thus, the **Grove cell** consists of a plate of zinc immersed in dilute sulphuric acid and *one of platinum immersed in strong nitric acid*, the two liquids being separated by a porous cell. The **Bunsen cell** is identical with the Grove, save that carbon is substituted for platinum. *In both cases the hydrogen that tends to appear* at the unattacked electrode is oxidised by nitric acid, and serves as a direct source of increased E.M.F. in the manner described above; since, however, the reaction causing the oxidation of the hydrogen involves separation of no substance possessing (as does the copper in the Daniell cell) any considerable amount of chemical energy, a larger E.M.F. (1·9 to 2 volts) is obtained, and a more complete conversion of the chemical energy of the zinc into electrical energy is secured.

Other materials that are unattacked by strong nitric acid—*e.g.*, iron and aluminium—may be substituted for carbon or platinum, but are generally less convenient and reliable.

Chromic acid is sometimes used as a depolariser and as an oxidant for the hydrogen, and has the advantage of being available in a simple cell, because, unlike nitric acid, it has no violent action on zinc and can be allowed direct contact with this metal as well as with the opposing plate, usually carbon; thus a **bichromate cell** in its simple form consists merely of a zinc plate and one of carbon immersed in a solution of chromic acid, to which has been added sulphuric or hydrochloric acid. An E.M.F. of about 2 volts *is thus obtained, and the internal resistance* of the cell may be made very low, as no septum is requisite. But as the zinc dissolves to some extent, if exposed to the chromic acid mixture, even when no current is being used, a porous pot surrounding the carbon and containing chromic acid solution is

an advantage, the zinc in this case being immersed in dilute hydrochloric acid. If the porous pot is dispensed with, the *zinc is always withdrawn from the solution when the battery is* not in use. Such "plunging" batteries are used for discontinuous work. The oxidation of hydrogen by chromic acid *results in the formation of chromic sulphate* when sulphuric acid is present, and chromic chloride when hydrochloric acid is used. In the former case, should bichromate of potash have been taken as the source of chromic acid, hard crystals of chrome alum ($KCr(SO_4)_2 . 12H_2O$) are formed and adhere to the plates, impeding the action of the battery. The use of chromic acid, or of hydrochloric acid in place of sulphuric acid, is, therefore, *preferable*.

A form of cell in which a **solid depolariser** is used is the **Leclanche,** which consists of zinc immersed in a solution of ammonium chloride, and carbon, surrounded with fragments of manganese dioxide, in the same solution. The function of the manganese dioxide is to oxidise the hydrogen which would otherwise appear at the carbon: the lower oxide of manganese *thus produced is re-oxidised by atmospheric oxygen, which thus* becomes the true depolariser. The fact that the Leclanché cell, when used for a considerable output of current, speedily becomes exhausted and recovers its efficiency on standing, lends support to this view of the action of the manganese dioxide. The chemical reaction concerned in the dissolntion of zinc in ammonium chloride results in the formation of zinc chloride, ammonia, and hydrogen. The last named is oxidised as stated above, whilst the ammonia and zinc chloride when present in considerable quantity, as in an exhausted battery solution, combine to form the compound $ZnCl_2 . NH_3Aq$, which separates in needle-shaped crystals. The E.M.F. of a Leclanché cell is about 1·4 volts.

Zinc is sometimes used in alkaline exciting liquids, this plan being feasible on account of the solubility of zinc oxide in caustic alkalies. A cell of this type is formed by zinc in caustic soda and carbon in the same liquid, the depolariser being cupric oxide, which is reduced to metallic copper. The E.M.F. is comparatively low—under 1 volt.

Whenever zinc is used in a galvanic cell, excited by an acid liquid, it is economical to amalgamate the zinc—that is, to coat it with mercury. The reason for this treatment is that commercial zinc contains impurities, notably lead, which are electro-negative to it, and with it form local couples which cause the dissolution of the zinc without contributing to the main output of electricity. The action of the mercury appears to be to dissolve the surface layer of the zinc, and thus to render all parts uniform in texture

and composition. The difference in behaviour between amalgamated zinc and zinc not thus treated is shown by the fact that when immersed alone in dilute sulphuric acid the amalgamated zinc is not perceptibly attacked, whereas the unamalgamated metal is freely dissolved.

In a properly arranged cell the chemical energy of zinc can be almost completely converted into electrical energy, but the money cost of the zinc, together with that of the necessary exciting and depolarising liquids, is prohibitory of its employment as a source of energy on a commercial scale.

A comparison of the energy available for mechanical work obtained by burning zinc in a galvanic cell and carbon beneath a boiler, gives the following results :—65 grams of zinc used in a Daniell's cell (which would probably cost least of all known combinations, for depolarising solutions) will give electrical energy equal to 50·1 Cal.* This is convertible, with a loss not exceeding 10 per cent., into mechanical work by the use of an electric motor, the final output being, therefore, an amount of mechanical work equal to 45·1 Cal. The same weight of carbon will give 520 Cal. when burnt; about 10 per cent. of this energy —that is, 52 Cal.—is convertible into mechanical work through the medium of a boiler and steam engine. From this it will be seen that, even were the cost of carbon and zinc per unit weight identical, the balance of advantage would be on the side of the carbon; as a fact, the cost of zinc is about fifty times that of carbon in the form of coal, a relation which shows that the commercial adoption of zinc as a source of energy is impracticable.†

Attempts to utilise the chemical energy of iron for the direct production of electrical energy have led to but little result, on account of the impossibility of amalgamating iron and the consequent uncontrollable rate of dissolution in acid which occurs when iron is used as the attackable plate of the cell.

Aluminium, when used as a source of electrical energy, has the advantage of a high heat of oxidation, a high valency, and low atomic weight (involving a large output of energy for a small weight of metal), and a low specific gravity. It is difficult of application, because when amalgamated its rate of dissolution is increased instead of being controlled.

* If oxidised directly without causing the reduction of an equivalent of copper, an increased output—viz., 85 Cal. (Zn,O = 85 Cal.)—would be obtained, but no cell is known which is capable of using air as a depolariser for continuous working.

† Since the product of the oxidation of zinc (ZnO) is of more money value than that of the oxidation of carbon, projects have been formed to prepare zinc white by the oxidation of zinc in a cell, utilising the electrical energy as a bye-product, but they have not proved remunerative.

There is no inherent reason why the chemical energy evolved by the oxidation of carbon should not be directly converted into electrical energy. If this could be done with even moderate success, a higher output of mechanical work than the 10 per cent. now commonly obtained from the combustion of coal, could be readily achieved, for the use of an electric motor allows of an output of about 90 per cent. of the energy supplied to it. Attempts in this direction have already been made. The type of apparatus used consists of a carbon plate immersed in fused sodium nitrate, opposed to an iron plate in the same liquid. Under these conditions the carbon is oxidised at the expense of the nitrate, whilst the iron is only superficially attacked. An output of about 30 per cent. of the calculated possible quantity of electrical energy has been thus obtained. The chief difficulties in utilising such an arrangement are the irregular oxidation and disintegration of the carbon. It is obvious that the nitrate is used pending the achievement of success in employing the oxygen of the air as an oxidant for the carbon: the cost of the process is much enhanced by this use of a comparatively expensive form of oxygen.

A **secondary cell** is one which can be regenerated, after it has furnished its full output of current, by the passage of a current from an external source in the reverse direction to the original current: the original condition of the plates is thus restored, and the cell made fit for a further output; such a cell can be used for the storage of energy (**storage cell**).

Any one of the **primary cells**, such as have been described above, if depending for its action upon chemical changes which can be reversed by the passage through the cell of a current of electricity from an external source, in a direction the reverse of that taken by the current generated by the cell itself, can be employed as a secondary or storage cell (**accumulator**). Those cells in which zinc is the attacked metal (unless used in alkaline solutions) are not suitable for employment as secondary cells, because zinc is not readily deposited from a solution containing a mineral acid, so that the chemical change induced by a reversed current will take the form of the decomposition of the water in the cell, and will not go so far as the reduction and regeneration of the zinc. In the case of a compound primary cell, the regeneration of the depolariser is also requisite if the cell is to be used as a secondary cell. This is impracticable with nitric acid and chromic acid cells, but it is possible with a cell using copper sulphate as a depolariser; nevertheless, the Daniell cell is not reversible because the zinc cannot be reduced in the acid solution. The cell consisting of zinc in caustic alkali, and carbon in the

same liquid, with CuO as a depolariser, is, however, reversible, inasmuch as zinc can be deposited from an alkaline solution.

The only form of storage battery of commercial importance is that in which lead is used as the attackable metal, and lead peroxide as the depolariser. A cell of this class resolves itself, therefore, into a plate of lead covered with spongy lead, opposed to a second plate of lead covered with lead peroxide, the two plates being immersed in dilute sulphuric acid (specific gravity, 1·18). When this cell is allowed to supply a current by closing the circuit between the electrodes, the spongy lead is oxidised and the lead peroxide is reduced; in each case lead sulphate is the final product. The E.M.F. produced by this chemical change is between 2 and 2·2 volts. Assuming the complete conversion of the surface of both plates into lead sulphate by the discharge of the cell, the calculated E.M.F. is over 3 volts, whilst if the spongy lead plate be alone converted into lead sulphate, an E.M.F. of about 2 volts should result. It is probable that, owing to the insolubility of the sulphate, a coating of the lead or the lead oxide with lead sulphate takes place, and the conversion on both plates is not complete, causing the production of an E.M.F. intermediate between these calculated limits.

Many forms of lead and lead peroxide secondary cells have been devised, but their difference is mechanical rather than chemical. The fundamental type of secondary cells is the PLANTÉ, in which the formation of spongy lead and lead peroxide on opposing plates is effected by "forming" the cell by alternately charging it from a dynamo and discharging it; these repeated reversals gradually convert the lead into a spongy state, suitable for rapid oxidation and reduction. The modifications of this fundamental form include cells of the FAURE type, in which the spongy lead and lead peroxide are produced by the electrolysis of lead oxide (generally red lead) applied as a paste to the surface of the lead plates; and modifications of this, in which the active material is held in recesses in a lead grid, or as plugs in a skeleton lead plate, have been devised.

The efficiency of a good secondary cell is about 80 per cent., reckoned on the electrical energy put into it. In spite of this good result, the commercial efficiency is often low, from the cost of repairs, due to the buckling of the plates and separation of the active material from its support. Where accumulators are used as a portable store of energy, their great weight—due to the high specific gravity and atomic weight and comparatively low valency of lead (Pb″)—is seriously detrimental. In spite of this, no metal has hitherto been found effective as a substitute for lead, entirely for chemical reasons.

Another form of storage battery, not yet of practical importance, is that known as **Grove's gas battery.** If a current of electricity be passed into an ordinary voltameter, consisting of two platinum plates immersed in dilute sulphuric acid, and if, after some decomposition of water into H_2 and O has taken place, the platinum electrodes be disconnected from the source of current and coupled to the terminals of a galvanometer, it will be found that a current is generated in the voltameter, and flows in a direction the reverse of that of the charging current. This is due to the fact that each platinum electrode absorbs a portion of the gas (*H and O respectively*) *evolved at its surface*; *the hydrogen* contained in the one platinum plate behaves as the attackable metal of an ordinary cell, whilst the oxygen in the other plate acts as the depolariser of the same cell. The condition and action of the plates of this cell are perfectly analogous to those *of the plates of a lead storage battery. The* quantity of energy which can be thus stored is limited by the amount of H and O absorbable by the platinum plates, which for plates of ordinary dimensions is small. By the use of a platinum plate coated with platinum black and supplied with hydrogen, opposed to a similar plate supplied with oxygen, both in contact with an electrolyte—*e.g.*, dilute sulphuric acid—a constant current can be maintained, the E.M.F. of which corresponds with that calculated from the heat of combination of the elements of water.

An attempt has been made by Mond to utilise this form of cell for the direct conversion of the chemical energy of hydrogen into electrical energy. The hydrogen for this purpose is prepared from semi-water gas (*q.v.*) by removing the CO and hydrocarbons, which it contains in addition to hydrogen. This is done by passing the gas over pumicestone coated with finely-divided nickel or cobalt at a temperature of 350° to 400° C. = 662° to 752° F. in the case of the former, and 400° to 450° C. = 752° to 842° F. for the latter; the chemical reactions involved are of the form—

$$2CO + Ni_x = Ni_xC + CO_2 \text{ and } C_mH_n + Ni_x = Ni_xC_m + H_n$$

When the pumice coated with nickel has become clogged with deposited carbon, it can be revivified by the passage of steam according to the equation—

$$Ni_xC + 2H_2O = Ni_x + CO_2 + 2H_2.$$

By such means, gas containing 36 to 40 per cent. of H, and almost completely free from CO and hydrocarbons, can be obtained.

This gas is supplied to a form of gas battery consisting of thin platinum leaf, finely perforated and covered with a film of platinum black, separated by a diaphragm of plaster of Paris (which is saturated with dilute sulphuric acid) from a similarly prepared platinum leaf; the second leaf is supplied with air, which serves as the depolariser. A current corresponding with about 50 per cent. of the calculated chemical energy can be thus obtained. Hourly reversals of the direction of the passage of the air and hydrogen, and, therefore, of the current, are necessary to prevent the transference of the sulphuric acid from one side of each cell to the other by electric osmosis.* The costly and delicate nature of the apparatus required is against the successful application of this method.

One other instance of the use of a gaseous depolariser is afforded by the chlorine battery, in which gaseous chlorine is applied as a depolariser to a carbon electrode in an ordinary cell.

Edison's secondary cell consists of iron and nickel plates or iron and nickel-cobalt plates in a caustic soda electrolyte. This cell has not yet been practically successful.

Formerly, the only method used on a considerable scale for obtaining electrical energy from the chemical energy of fuel was that in which the fuel is burnt beneath a boiler which supplies steam to an engine, which in turn drives a dynamo. The chemistry of steam-raising will be treated of below. At present, it is often more economical to use gas engines with the necessary producers. Decision between the use of a steam and gas plant depends on conditions proper to each case; no general directions can be given. A point of much importance connected with the economy of the dynamo is, however, of chemical interest, and must be mentioned here. It has been found that the efficiency of the iron used for field magnets and armatures of dynamos varies with its magnetic properties; the more rapid and complete its magnetisation and demagnetisation, the better the results obtained. No quantitative relation has yet been arrived at for the influence of the impurities present in commercial iron on its magnetic properties; but, qualitatively speaking, the more nearly pure the iron, the greater the rate of magnetic change and the smaller the amount of residual magnetism which it retains. A full discussion of this matter would be out of place in a work of this scope. The selection of a suitable metal or alloy for the commutator and brushes of the dynamo is obviously also a chemical matter.

* This term is applied to the bodily transference of an electrolyte through a porous septum; this is caused by the passage of a current, and takes place in the direction in which the current flows.

NATURAL FORMS OF KINETIC ENERGY.—The foregoing examples of sources of energy available for industrial purposes are instances of *potential energy capable of becoming kinetic* when subjected to suitable conditions. They are examples of a *particular kind of energy—namely, chemical energy*—and, generally, the first step to their utilisation is their conversion into heat. *In less general language they are cases of the energy of* fuel which is available for the production of heat by direct burning. In those sources of energy which we are about to consider, the energy is not potential but kinetic—that is, it is actually in course of being expended without the intervention of human agency, and its utilisation can, therefore, be less easily regulated than that of the energy which is locked up in fuel. A concrete case of a form of kinetic energy which exists on the earth and is put to industrial use, is that manifested in a river or a waterfall. It is certain that the energy represented by the flowing water will be expended whether it be turned to commercial account or not, whereas a seam of coal is a form of energy stored in a manner so perfect that it may remain potential for an indefinite period, provided it be not mined and burned. The chief natural forms of kinetic energy are as follows:—

Water Power.—Water power has been used from early times to drive flour mills; in more recent times it has been used to work saw-mills. At present the generation of electricity is by far its most important use. Running water of all kinds may be utilised for obtaining energy in an applicable form. The main conditions of success and economy are that the quantity shall be large, the fall in a given length of the watercourse considerable, and the flow approximately constant. The mean quantity per unit of time cannot usually be artificially increased, but the fall within a given distance can be augmented by the device of forming a dam or weir, and this is commonly done with streams supplying water wheels. The fall may also be increased by excavating the river bed below the rapids, and this has been done in several places in Scandinavia. The regularity of flow can be aided, though not completely secured, by retaining the water in a reservoir large in proportion to the amount used per day; but, in general, intermittently flowing water is of little industrial value. Where the fall is sudden, as in an actual rapids or waterfalls, it is sometimes impracticable to use the bed of the stream itself for the wheel or turbine, and the water must be diverted and provided with a less precipitous channel. Thus at Niagara the water is led into a special channel in which the turbines it is to drive are disposed. Water power is sometimes situated conveniently near mineral deposits which need energy in the form

of mechanical power for their working, and it can then be used economically. This is the case in some copper refineries where the electrolytic process is used (see *Copper*). One of the oldest instances of the application of water power to the winning of a metal is in the works of the Aluminium Company at Neuhausen, where the energy requisite to drive the dynamos, the current from which is used in the reduction of aluminium, is derived from a waterfall. In a similar manner aluminium is now made at Foyers in Scotland, at Niagara, and other places. Calcium carbide (see Vol. II.) is made in many places by energy derived from water power. The manufacture of artificial fertilisers from atmospheric nitrogen is practically dependent on cheap hydro-electric power, and fairly large works are established in Norway and Italy. In mountainous countries, railways (*e.g.*, the Simplon tunnel line) are worked, and towns (*e.g.*, Innspruck) lighted by electricity derived from water power. Industries that are not conveniently carried out on the spot where water power is available may, nevertheless, obtain the energy they require therefrom; this is economically effected by converting the water power into electricity, and transmitting high tension currents, which can be used after their conversion into currents at a low pressure, the need for massive copper conductors (in which much capital would be sunk) being thus overcome. Thus, the Victoria Falls in Rhodesia are to supply the gold mines of the Transvaal with power.

Tides.—Although at first sight only a particular case of water power, tidal energy must be considered separately, as it is derived from a source different from that represented by a stream or waterfall. All the forms of energy that have been dealt with in this chapter—with the possible exception of the chemical energy of petroleum, which may have been derived from the cosmical energy left stored in the earth at the time of its condensation from a nebulous to a fluid condition—are simply forms of solar energy, which has first appeared in some form of life on the surface of the earth, and has been afterwards stored in its crust. This is true, because coal is used almost exclusively for the production of mechanical from chemical energy. Admitting the animal origin of petroleum, which theory has much to recommend it (see *Petroleum*, Vol. II.), the energy present in it would also be referred to the sun. But the energy of the tides is due to the energy of rotation of the earth, sufficing to keep it in motion in spite of the breaking action of the mass of water attracted into a huge wave by the moon; every motion of the sea which is tidal and not due to the wind, is of this origin. Consequently, when tidal energy is turned to a mechanical account, power is being

taken by, as it were, putting a driving belt on the globe, albeit one in which there is a good deal of slip. Hitherto no great success has attended attempts to utilise tidal energy, the range of motion is generally too small, or, if increased by local conditions, such as the bore of a river, too violent and intermittent to allow of steady work. Perhaps the most hopeful method consists in impounding a large quantity of water at high tide, and using it as one would use that from any other reservoir with an available fall. Tidal energy has, of course, been used for ages in the somewhat crude way of aiding the transport of vessels against a running stream near its mouth.

Wind.—In spite of the variable and intermittent character of the energy that can be obtained from the motion of the air, it is capable of commercial utilisation, and has been so utilised from early times by means of windmills of various design. It is self-evident that if any considerable industry were to be made dependent upon wind power, it would be necessary to collect the energy represented by a large cross-section of the mass of moving air, which we speak of as wind, and to store the energy thus got to provide for the occurrence of a calm. This has been realised on a small scale by the application of windmills to pumping for draining operations and the storage of the water, or for driving a dynamo and storing electrical energy in accumulators (*v.s.*).

Sun's Heat.—Energy is continually being poured upon the earth from the sun, and is being stored to some slight extent in the liberation of carbon from carbon dioxide by vegetable life,* but is for the most part returned to space by radiation. Numerous attempts have been made to turn it to account by causing it to boil water or other volatile liquid, mechanical work being obtained by the expansion of the vapour of this liquid; but the radiant energy, even when concentrated by a system of mirrors or lenses, is too diffuse and, moreover, too intermittent to be of any tangible use.† The only serious application on any considerable scale is in concentrating solutions of salt from sea water, or, in countries destitute of fresh water, distilling sea water for drinking purposes. It has been suggested that the internal

* It has been calculated that 1 square metre of leaf surface will utilise sufficient radiant energy from the sun per day to fabricate 14 grams of dry vegetable substance. Fischer calculates that on 140 days of the year about 5 per cent. of the sun's energy received on the area covered by the German forests is utilised in growing the trees. In the tropics the proportion may be much greater.

† A small pocket lens may be utilised to light tobacco on a windy day at the sea-side.

store of heat in the earth may be tapped for conversion into mechanical energy.

Value of Natural Forms of Energy.—We have spoken of natural forms of energy, although all energy is natural, in a sense restricted to those cases where kinetic energy occurs in nature. The value of natural kinetic energy may be looked at from two points of view. In the first place, since it is kinetic it will be inevitably degraded into low temperature heat, and it is good economy of the total store available on the earth to turn it to account on its downward path, instead of letting it run wholly to waste. But, in the second place, since its utilisation involves the use of costly plant, it is often commerically economical to disregard it utterly, and rely wholly on the stores of energy in the shape of fuel in one kind or another that wonld otherwise remain stored for an indefinite time. The circumstances of each case must decide which course is attended by the greater monetary economy; it suffices to say here the course chosen is not necessarily most economical from an energy point of view. There are many important industries in which the energy required is a small part of the money cost of the whole process, and economy in the energy bill is a secondary matter altogether, and may be sacrificed to convenience or lowness of initial outlay.

The Transmission of Energy.—This chapter would be incomplete without a few words concerning the different methods of transmitting energy that are commonly used. The simplest way of communicating mechanical energy from one moving object to one that is to be moved, is by direct attachment. In the case of a revolving wheel, where the axis of rotation of the wheel to be moved is identical with that already moving, a shaft of the requisite length is an obvious method: where the axes of rotation are not identical, driving first by frictional contact with the rim, and then by regular rugosities on the rim—*e.g.*, teeth or cogs—suggests itself. A step farther is the transmission of power by belts or ropes, and these are of course freely used. Ropes running at a high speed, and, therefore, capable of transmitting a good deal of energy without severe pull, are a fairly economical method of distributing power. Water under pressure is another plan that has merits in cases where strong slow motions are especially required, as in most hydraulic machinery, but is less well adapted for any quick-running motion, as the friction and inertia of water transmitted through pipes are serious obstacles. Air has fewer disadvantages as a fluid for transmitting power, but energy is lost in compressing it, heat being developed which is dissipated before it reaches the point of consumption. Where any extensive system of transmission of

energy by compressed air is in use, it is commonly supplemented by some method of heating the air from an external source before it is used to drive its motor (see p. 79). The best method of transmission through a considerable distance that has hitherto been devised is by the use of electricity. The general plan consists in turning the mechanical energy developed by a steam engine into electricity at comparatively low electrical pressure, converting this by means of a step-up transformer into electricity at high electrical pressure, transmitting through a conductor in the ordinary way, and re-converting it, on the spot where it is to be used, into electricity at low pressure by means of a step-down transformer. Operose as this sounds, it is fairly economical, the least efficient part being the prime mover (that is, the engine and boiler), which has to be employed in any case. The object of using the current at high pressure for the actual transmission, is that the loss by the resistance of the conductor is smaller with a high-pressure than with a low-pressure current, and thus a large conductor of low resistance, which is a very costly piece of plant because of the comparatively high price of copper, can be dispensed with.

CHAPTER III.

THE CHEMISTRY OF STEAM RAISING.

IN modern engineering practice, which is concerned with obtaining mechanical energy from fuel by means of a boiler and engine, much care is displayed in points of design and construction, whilst, on the other hand, but scanty attention is paid to the economical working of the plant, which depends in great measure on purely chemical principles.

WATER.

Next in sequence to the chemical principles concerned in the combustion of the fuel, which are obviously of primary importance and have been dealt with in the preceding chapter, stands the quality of the water used in the boiler; its selection demands careful consideration by the steam-user. Since the general town supply of water for any particular place has been chosen—and filtered or otherwise purified—chiefly in order to fit it for drinking and domestic use, it is often too costly for employment for feeding boilers and other industrial purposes, particularly as the properties which render it suitable for dietetic use are not identical with those characteristic of a good boiler water; recourse is, therefore, had to a private well, the nature of the water of which must be ascertained by analysis, and then a correction devised for any deleterious action which may be exerted by the water on a boiler, or by the steam in its utilisation, owing to any matter it may carry over in suspension or as a vapour. Most waters which are used for steam raising fall in one of the following classes:—

1. Hard calcareous waters.
2. Soft peaty waters.
3. Saline waters.

This division is not strictly accurate nor exhaustive, as the classes may overlap to some extent, but it serves to define the most commonly occurring waters which are used for steam raising. The source of the supply has a certain relation to the quality of the water, since the strata from which it is derived

furnish characteristic soluble constituents to the water percolating through them. It happens, therefore, that where it is possible in choosing a site for a factory, to pay regard to the surrounding strata, a water of approximately known quality can be procured; thus the chalk formation is sure to yield a hard calcareous water, the same being true of oolitic and other limestone strata: whereas the formations known as the lower greensand and the new red sandstone, generally yield waters which are comparatively soft. Since other circumstances, such as facility of transport, cheapness of fuel, and the like, usually determine the site of a factory, the choice of particular strata whence to obtain water is rarely practicable, and it becomes necessary to deal with whatever variety of water may be locally predominant.

Taking the classes mentioned above *seriatim*, the following descriptions may be given:—

1. **HARD CALCAREOUS WATERS.**—The most characteristic constituent of these waters is calcium carbonate, often associated with magnesium carbonate, both salts being held in solution by carbonic acid. The solvent action of carbonic acid on these carbonates is so marked that it is attributed by some to the formation of bicarbonates (analogous to those of the alkali metals) of the form $CaH_2(CO_3)_2$. It must be noted, however, that the quantity of CO_2 present is almost invariably greater than that which would suffice for the formation of bicarbonate; nevertheless, on the Continent it is customary to indicate that portion of the carbonic acid corresponding with the carbonates which it is instrumental in retaining in solution, by the term "half-bound," to distinguish it from the surplus which is termed "free." Whatever the precise mechanism of the solvent action of carbonic acid on calcium and magnesium carbonates, these salts are invariably precipitated nearly completely when the carbonic acid is expelled by boiling.

In addition to calcium and magnesium carbonates, hard calcareous waters commonly contain calcium sulphate, which is not precipitated on boiling under atmospheric pressure, although when the temperature of the water is considerably above 100° C. = 212° F., as in a boiler, precipitation of anhydrous calcium sulphate, $CaSO_4$, takes place. The crust of calcium sulphate and carbonate deposited at the temperature obtaining in a boiler which is worked at even a moderate pressure, is hard, dense, and coherent, and much impedes steam raising, as will be noticed later.

In the absence of calcium sulphate, calcium carbonate generally yields a pulverulent deposit, less objectionable than that given by a water containing both salts. The following are analyses of typical boiler incrustations from hard calcareous waters:—

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
$CaCO_3$, ...	55·65	...	81·10
$CaSO_4$, ...	31·96	97·01	9·86
$Mg(OH)_2$, ...	7·11	0·37	2·58
Water, ...	...	1·75	...
Fe_2O_3 and Al_2O_3, ...	2·10	...	1·48
Silica and insoluble matter, . .	2·46	...	3·54

It will be seen that even at the moderate pressure of 50 lbs. (which is that at which the above incrustations were formed) calcium sulphate is freely precipitated. The occurrence of magnesia in the form of hydroxide in the incrustation, will be discussed in a later paragraph.

It is customary to speak of water containing salts of calcium and magnesium as "hard," the term being especially used as indicating their soap-consuming power when such waters are employed for washing—a hard water being one which consumes much soap before a lather can be produced in it. The first action of soap on a hard water is to precipitate calcium and magnesium salts of the fatty acids of the soap. The curdy precipitate thus formed is useless as a detergent, and it is not until the soap itself passes into solution that a lather is produced, this lathering being a characteristic property of a soap solution. A distinction is usually drawn between **temporary hardness** and **permanent hardness.** The former is caused by the presence of calcium and magnesium carbonates, which are precipitated in great measure when the water is boiled, and on this account may be considered as temporary hardening agents. The latter is due to the other salts of calcium and magnesium which are not precipitated when the water is boiled—*e.g.*, the sulphates, chlorides, and nitrates; with regard to calcium snlphate it must be remembered that it is precipitated when the water is heated to a temperature above its normal boiling point—that is, under pressnre in a boiler. It follows from this that the mere statement of either temporary or permanent hardness, or of both, is no guide to the character or amount of the boiler scale which will be formed, and a complete mineral analysis of the water is requisite, even this being only a guide towards the formation of an opinion by the chemist as to the behaviour of the water under conditions comparable with those obtaining in practice.

In general, hard calcareous water, producing much scale, is not liable to cause, in addition, corrosion of the boiler, both on account of its inherent qualities (see *Saline waters*), and because of the protective effect of the scale deposited.

The following analyses give the quantities of salts commonly found in hard calcareous waters :—

	Grains per Gallon.			
$CaCO_3$,	15·23	12·86	23·72	19·55
$CaSO_4$,	12·04	...	7·31	16·08
$MgCl_2$,	...	...	6·29	28·71
Na_2SO_4,	6·97	12·67	...	...
$NaCl$,	4·70	25·39	29·82	20·25

2. **SOFT WATERS** (containing little mineral matter).—Rain water collected artificially is a typical soft water, containing but a trifling amount of mineral matter in solution. Streams fed with rain water and running through districts containing little vegetation, yield a water standing near to rain water in respect of its content of mineral matter. The majority of soft waters, however, on account of the absence of calcareous matter, dissolve peaty matter from the vegetation which they encounter on their course. These peaty substances consist largely of vegetable acids, the calcium salts of which are insoluble in water, so that they are not dissolved by hard waters. Their feebly acid character renders peaty waters liable to attack boiler plates, and the slimy nature of the salts which are produced by such attack causes them to form an objectionable incrustation (*v.i.*).

As peaty waters, in common with all natural waters, contain dissolved oxygen, their action on metallic pipes and plates is enhanced by the fact that any oxide formed by the action of the dissolved oxygen is basic in character and will combine with the peaty acids, rendering the corrosion of the metal more serious. The action of the acids in this respect is similar to that of CO_2 in the attack of iron by atmospheric oxygen (see Chapter i., p. 46). Such waters are also peculiarly liable to act on lead.

The following are analyses of soft peaty waters :—

	I. Water of the Wye (Phillips). Grains per gal.	II. Moorland Water. Grains per gal.
$NaCl$,	1·04	1·07
$CaCl_2$,	0·06	...
$Ca(NO_3)_2$,	0·09	0·41
$CaSO_4$,	1·12	...
$CaCO_3$,	2·88	0·77
$MgCO_3$,	0·95	...
SiO_2, Fe_2O_3 and Al_2O_3,	0·26	...
Organic matter,	0·27	...
Na_2SO_4,	...	0·71

3. **SALINE WATERS.**—An extreme example of a saline water used for boiler purposes is sea water. The following analysis of water from the Irish Sea (*Thorpe*) represents the average composition of sea water; although considerable variations in concentration occur locally, the ratio of the salts to each other is nearly constant:—

	Parts per 1,000.*
$NaCl$,	26·44
KCl,	0·75
$MgCl_2$,	3·15
$MgBr_2$,	0·07
$MgSO_4$,	2·07
$CaSO_4$,	1·33
$CaCO_3$,	0·05
Iodine,	Trace

Waters which may be classed as "moderately saline," of course, vary considerably in composition. The following analysis represents a water of this class:—

	Grs. per gall.
$CaCO_3$,	3·18
$MgCO_3$.	2·14
Na_2CO_3,	12·81
Na_2SO_4,	19·33
$NaCl$,	19·08

When sea water is used in a boiler a concentration is soon reached at which the soluble salts begin to separate. This point is indicated by the specific gravity of the concentrated water, and for its determination it is customary to ascertain the specific gravity of the liquid in the boiler from time to time by means of an hydrometer called a **salinometer.** When this concentration is attained the water must be blown out. When very saline waters are used for steam raising the adoption of condensing engines is advantageous, as it allows of the return of the major part of the water which has passed through the cylinders as steam, to the boiler, and thus concentration to the crystallising point is greatly retarded.

Brackish water drawn from rivers (near their mouths) and from estuaries may be regarded as diluted sea water. A great objection to its use arises from its variable character, as its composition depends on the proportion of sea water locally and temporarily present. Since sea water contains calcium sulphate, which salt is deposited in a boiler (*v.i.*), it follows that, even when used to a concentration short of that at which the deposition of ordinary soluble salts begins, sea water will

* Thus stated, instead of in the more usual nomenclature (grains per gallon), on account of the great concentration of sea water as compared with ordinary saline waters.

yield an incrustation, the nature of which is shown by the following analysis (*Lewes*) :—

	Per cent.
$CaCO_3$,	0·97
$CaSO_4$,	85·53
$Mg(OH)_2$,	3·39
NaCl,	2·79
SiO_2,	1·10
Fe_2O_3 and Al_2O_3,	0·32
Organic matter,	Trace
Moisture,	5·90
	100·00

The presence of $Mg(OH)_2$ in the boiler deposit from sea water is caused by the decomposition of magnesium chloride at the high temperature obtaining in a boiler (the dissociation of this salt being readily effected on evaporation), and also by the decomposition of magnesium carbonate formed by the interaction of calcium carbonate with the soluble magnesium salts present in excess. Such portion of the magnesium hydroxide as results from the decomposition of magnesium chloride is a measure of the corrosive effect of this last-named salt on the boiler plates, for it will be obvious that the deposition of magnesium hydroxide involves the liberation of an equivalent quantity of HCl if its source be simply magnesium chloride without the intervention of calcium carbonate in the manner spoken of above. It is known *that magnesium chloride, when heated in presence of water,* readily decomposes into magnesium hydroxide or an oxychloride, and hydrochloric acid ; in aqueous solution this does not take place until considerable concentration has occurred, but it is probable that in a boiler dissociation is promoted by the higher temperature attained ; local over-heating of the salt, already separated from its solution on parts of the boiler above the water line, may also take place. These two actions suffice to *produce the corrosive effects observed, which, owing to the* volatility of HCl, may extend to all parts traversed by the steam —*e.g.*, steam pipes and cylinders. Local action caused by these circumstances may occur in spite of the feed water being alkaline from the presence of calcium carbonate, as the incrustation *formed by this salt will only afford protection below the water* line.

The subject of the action of magnesium chloride in boilers has aroused considerable interest during recent years. Bailey has found that in the distillation of $MgCl_2$ solution hydrochloric *acid does not appreciably* volatilise with the steam until a concentration of 1 per cent. is reached. Hence, injury to the boiler

plates will occur long before any acidity is apparent in the steam. The decomposition of $MgCl_2$ under pressure has been confirmed by Cribb, although he found it to be stable when boiled at ordinary pressures, even in the presence of iron filings. That $MgCl_2$ is almost entirely decomposed under the conditions prevailing in an ordinary boiler is proved by the disappearance of dissolved magnesia from boiler waters, and the appearance of magnesium hydroxide as one of the commonest constituents of boiler scale in which chlorine is rarely present except in traces. Cribb points out that the available evidence tends to show that chlorine does not leave the boiler, and that, therefore, the concentration of the chlorine is a measure of the concentration of the boiler water itself.

The *role* of $MgCl_2$ in the production of magnetic iron oxide Fe_3O_4 in the boiler has been explained by Dewrance as follows:— It is first decomposed with the liberation of free HCl—

$$MgCl_2 + H_2O = MgO + 2HCl,$$

the latter attacks the boiler plate, producing ferrous chloride and hydrogen—

$$Fe + 2HCl = FeCl_2 + H_2,$$

the ferrous chloride finally reacts with the MgO previously formed, producing again $MgCl_2$ and ferrous oxide—

$$MgO + FeCl_2 = MgCl_2 + FeO.$$

If there is a considerable excess of air the ferrous oxide is oxidised into ferric oxide, Fe_2O_3, but if the quantity of air present is not sufficient for this, then the magnetic oxide, Fe_3O_4, is formed.

A marine boiler incrustation will contain calcium sulphate as the chief constituent, and magnesium hydroxide as the main secondary constituent; the following analysis (*Lewes*) will serve as an example in addition to that on p. 136:—

	Per cent.
$CaSO_4$,	84·27
$Mg(OH)_2$,	7·04
Sand,	1·94
Fe_2O_3 and Al_2O_3,	1·10
Water, &c.,	5·65
	100·00

Many waters derived from mines contain large quantities of saline constituents, especially sulphates, often derived from the

oxidation of pyrites and other sulphides. The following analysis (*Allen*) is an example of a mine-water rich in sulphates :—

	Grs. per gallon.
$CaCO_3$, ...	10·8
$CaSO_4$, ...	16·0
$MgSO_4$, ...	20·4
Na_2SO_4, ...	73·6
$NaCl$, ...	70·4

When calcium carbonate is absent, free sulphuric acid often exists in waters of this class, leading to serious corrosion of pumping machinery.

The life of the boiler depends on several factors, of which the character of the water, considered above, is one of the chief. Hard calcareous waters form scale in the manner already described, and in this respect are injurious to the economy of steam raising, partly by damaging the boiler itself, and partly by wasting the fuel required. The latter is a serious evil, for the incrustation is a badly conducting material, and, by impeding the transmission of heat from the furnace to the water, diminishes the output of steam from the boiler, if the furnace is fired normally—that is, at a rate approximate to the absorption of heat by the "heating surface" exposed by the boiler. To compensate for this diminished output of steam, the natural action of the stoker (often necessary when the full output of the boiler is required) is to increase the rate of firing, with the result that the extra quantity of heat generated in the furnace is only imperfectly absorbed by the boiler, and goes to waste in the flue gases. It has been found that an incrustation of $\frac{1}{8}$ inch thick causes the use of about 16 per cent. more fuel than would be necessary with clean plates, whilst one which is $\frac{1}{4}$ inch thick involves a waste of as much as 50 per cent., and one of $\frac{1}{2}$ inch a waste of 150 per cent. The damage to the boiler itself is due to two causes—(1) the deterioration of the plates by overheating, and (2) the mechanical damage involved in removing the incrustation. A coated boiler plate is necessarily hotter than when clean, as the water is kept from free contact with it. Thus, whereas a clean iron vessel containing water boiling under atmospheric pressure has a temperature not more than 10° C. above the boiling point of water, one with an incrustation so thin as $\frac{1}{16}$ inch may have a temperature more than 100° C. higher. The mechanical properties of the metal composing the boiler plates are considerably modified even by the temperature proper to modern pressures—*e.g.*, 150 to 200 lbs. of steam, corresponding with 370° to 400° F. = 188° to 204° C.—and are still more affected when there is extra heating on account of the presence of an incrustation.

In the case of boilers of the water tube or of the locomotive class, a further difficulty arises from the incrustation—namely, the blocking of the tubes or of the spaces between them with scale, and consequent hindrance of circulation of the water. In aggravated instances actual stoppage of a water tube may occur, involving its speedy destruction by its exposure to the fire without being simultaneously cooled by contact with the water.

The nature of the incrustation formed in the manner already described may be modified by the presence of suspended matter, which often occurs in feed water from running streams. These impurities remain in the boiler and mix with the precipitated deposit. Very finely divided vegetable matter is not always objectionable, for it may help in keeping the deposits from caking hard. For this reason filtered waters are sometimes more troublesome than unfiltered. Earthy impurities are invariably objectionable, and may be dangerous. The clay which is usually present helps to form a hard scale.

The evils of heavy incrustation are sufficiently well recognised to lead to the practice of periodically chipping the scale from the boiler plates, a troublesome operation, liable to cause injury to the boiler, and best avoided by removing the cause of incrustation. Although a water yielding a heavy or even a moderate scale is thoroughly objectionable, one giving a slight film of calcium carbonate or sulphate is not wholly harmful, on account of the protection which it affords against corrosion from the several sources now to be mentioned.

When saline waters are used which contain calcareous salts, the incrustation formed and the damage caused will be similar to those arising from calcareous waters proper. As magnesium chloride is frequently present in saline waters, a corrosive effect on the boiler also occurs from the cause described above. In addition to magnesium chloride other salts are capable of reacting with the production of acids which may cause corrosion. Ferric and aluminium salts, for instance, under the influence of heat may give rise to basic salts and free acids. A large number of such possible reactions has been given by H. de la Coux, and the following equations are given as typical instances :—

$$Al_2(SO_4)_3 + 3H_2O = Al_2O_3 + 3H_2SO_4$$
$$Fe_2Cl_6 + 3H_2O = Fe_2O_3 + 6HCl$$
$$(NH_4)_2SO_4 = 2NH_3 + H_2SO_4$$
$$2Fe_2(SO_4)_3 = (Fe_2O_3)_2SO_2 + 5SO_3.$$

Sulphuretted hydrogen may also occur, especially in canal waters contaminated with sewage, or with furnace ashes or

refuse, or in some waters from coal measures. Such waters are liable to cause corrosion by reason of the oxidation of the sulphuretted hydrogen to sulphuric acid. Such corrosion will not take place below the water line if a protective incrustation be formed; but serious weakening of the boiler will result from the attack of the plates above the water line, since the corrosion is not uniform, but local, for a reason stated below. Of course, mine-waters in which free acid is present will cause serious corrosion, and must be treated before use, particularly if containing the salts of metals reducible partially or entirely by iron—*e.g.*, Cu, and Fe in the ferric state. With copper salts the copper is first reduced at the expense of the iron of the boiler, and then forms with the plate an iron-copper couple, of which the iron is the attackable metal. With regard to ferric salts, direct reduction to ferrous salts, necessitating the solution of an equivalent of iron, takes place, and if oxygen be present the ferrous salts formed by this reduction act as carriers between the oxygen and the iron of the boiler.

Soft waters which cause no incrustation, save that due to peaty matter—concerning the action of which but little authentic information has been obtained—and having but trifling saline constituents, are nevertheless liable to cause damage by corrosion. As all natural waters that have been freely exposed to the air are nearly saturated with oxygen, the quantity present being, at 15° C. = 59° F., 10 mgms. per litre,* all would be liable to cause oxidation of iron in a boiler, were it not that those which are calcareous form a protective incrustation which diminishes the damage done. In the case of waters not yielding an incrustation—*e.g.*, soft peaty waters—the influence of dissolved oxygen on the metal of the boiler is more marked, its action being identical with that of ordinary rusting (*q.v.*)—(*cf.* p. 45).

Corrosion chiefly occurs at the water line, the reason apparently being that the oxygen is rapidly expelled from the water

* This limit of saturation is, of course, influenced by the partial pressure of O in air. A higher figure is given by pure oxygen. The following table shows the solubility in c.c. per litre of water of the three chief gases normally present in water at various temperatures and at a pressure of 760 mm. exerted by each gas :—

	0° C. = 32° F.	*10° C. = 50° F.*	*20° C. = 68° F.*
O, . . .	42	33	28
N, . . .	20	16	14
CO_2, . .	1,797	1,185	901

on heating and then attacks the iron where it is wet but not covered with water: a second cause, having a like effect, is the tendency of the bubbles as they are expelled during the heating of the water, to cling to the sides, especially at the surface. It will be remembered that the gases dissolved in water are relatively richer in oxygen than is the air from which they have been derived, the ratio of O to N being approximately 1 : 2; this circumstance enhances the corrosive action.

In view of experiments showing that steel wire which has been exposed to boiling water (at 760 mm.) has a lower tensile strength than that which it previously possessed (a diminution of about 20 per cent. in 84 days), it appears probable that, in the absence of an incrustation, a similar weakening of the boiler plates may occur. The cause of this alteration is probably the decomposition of a portion of the water at the temperature of the boiler by the iron, and the absorption of the hydrogen resulting from that decomposition, for it is known that iron which has absorbed hydrogen is more brittle than the metal in its ordinary state (see Footnote, p. 32).

A form of incrustation which is peculiarly harmful both to the economical working and to the life of a boiler, is that formed when oily matter obtains access to the feed water, and thence passes into the boiler. When animal or vegetable oils are used as lubricants in the cylinders of the steam engine (see *Lubricants*), hydrolysis of the oils may occur by the action of the high-pressure steam, aided by the presence of metallic oxides from the material of the cylinder, and fatty acids may be volatilised with the exhaust steam into the condenser of the engine, and thus pass with the feed water to the boiler. Even when mineral oils are used as lubricants and no hydrolysis can occur, a portion of the mineral oil may be distilled over with the steam, in spite of the temperature of the cylinder being below that at which distillation occurs when the mineral oil is heated *per se*, and may similarly find its way into the boiler. In the case of fatty oils, the acids derived from them form lime soaps with the lime in calcareous boiler water, and are deposited in this form as an adherent oily incrustation, very badly conducting in character. Mineral oil, on the other hand, will attach itself mechanically to calcium carbonate and sulphate during their deposition from the water, forming with them oily globules which eventually coat the plate with a non-conducting incrustation. Thus, in either case, the plates are more thoroughly protected from contact with the water, by reason of the oily character of the incrustation, than is the case when the incrustation is purely calcareous. Overheating and collapse of plates thus consequently

take place. A scale of this kind was found by Lewes to have the following composition:—

	Per cent.
$CaSO_4$,	59·11
$CaCO_3$,	6·07
$Mg(OH)_2$,	11·29
$Fe_2O_3.Al_2O_3.SiO_2$,	2·85
Organic matter and oil,	19·54
Moisture,	1·14
	100·00

The general process of corrosion is identical with that described under the rusting of iron (see p. 45). The two main theories which are held to-day concerning this process are known as the "acid" and "electrolytic" theories respectively. According to the former, no rust can be formed from pure water, oxygen, and iron, but the presence of a trace of some acid to act as catalyser is absolutely essential if oxidation of the metal is to begin.

On the other hand, the electrolytic theory says that the presence of an acid, even in traces, is not essential to the oxidation of the iron, liquid water, and oxygen alone being necessary. It is assumed that pure water is ionised to a small but definite extent, and that when iron comes in contact with it positively charged Fe ions are sent out into the water. Hydrogen ions at the same time leave the liquid, which latter now becomes virtually a solution of ferrous hydroxide—

$$Fe + 2H^{\cdot} + 2(OH)' = Fe^{\cdot\cdot} + 2(OH)' + H_2.$$

The presence of oxygen will now cause the oxidation of ferrous iron to the ferric condition and rust appears.

The question whether pure water is sufficiently active to cause the corrosion of iron in this way is not yet definitely settled. Although the two theories are apparently conflicting, it is interesting to notice that in the electrolytic theories water itself is regarded as a feeble acid, since it contains hydrogen ions. Either view is in harmony with the modern electrolytic theory of ionisation, and the solution of the problem is of theoretical rather than practical value.

The evidence accumulated from such investigations as those of Cushman, Walker, and others snpports the contention that all substances in solution containing hydrogen idns (*i.e.*, of an acidic nature) stimulate rusting, while hydroxyl (OH) ions to a certain extent inhibit it, and if the concentration be sufficient, absolutely prohibit it.

Certain points regarding the nature and mechanism of the

corrosion to which a boiler may be subjected need separate mention. Thus, local corrosion or "pitting" is liable to occur. By this term is meant the formation of small hollows or depressions in the boiler plates indicating rapid local attack, which may lead to the necessity for renewing a much larger area than that which is actually damaged. The cause of this local action is to be found either in the composition of the attacked plate, or in the nature of the mode of attack, or in both. A plate of ingot-iron such as is used for boiler making, may have its impurities, notably manganese and sulphur, irregularly distributed throughout its mass. Spots rich in these impurities will suffer corrosion more rapidly than other parts, possibly because of the formation of a galvanic couple between adjacent portions of the plate which are of different composition. Such a case of pitting in a boiler has recently been brought forward by G. N. Huntly. Each pit was found to be the centre of a blister, and the blister contained a slightly acid solution of ferrous sulphate, while the boiler water was alkaline with caustic soda. The solid matter in the envelope of the blister, which consisted of a mixture of iron oxides, acted as a semi-permeable membrane keeping apart the ferrous sulphate within and the caustic soda outside the blister. The theory advanced was that the particles of manganese sulphide, segregated in the steel, were oxidised by the oxygen dissolved in the boiler water to sulphuric acid and an oxide of manganese, the acid then acting locally on the surface of the boiler plate in the vicinity of the particles of manganese sulphide. The pitting of the boiler plate was prevented by adding sodium arsenite to the boiler water, the reagent taking up the dissolved oxygen. Similarly, the impurities, including the slag, which are characteristic of puddled iron (still sometimes used for boiler making), are not uniformly diffused through the metal, and the places richest in these impurities will be more readily corroded, the mechanical looseness of structure due to the presence of the slag often aiding this effect.

Irregularities in its physical condition, as well as in its chemical composition, will also affect the liability of iron and steel to corrosion. Strains produced by drawing or pressure may cause differences in chemical activity; hence plates with punched rivet holes have been found less permanent at these spots than plates with drilled holes. Differences in temperature at different parts of a boiler may also set up thermo-electric phenomena.

Pitting, when once started, continues, owing to galvanic action between the metal and previously oxidised iron. For this reason it is sometimes the practice, when pitting occurs,

to clean out the pits so as to remove all traces of oxide, and then brush mineral oil over the pitted places.

Particles of brass and copper finding their way into a boiler, sometimes act as centres of corrosion by setting up galvanic action in which the iron is the metal attacked. This is especially the case when most of the surrounding iron is protected by incrustation, the corrosive action being thus localised, consequent on the increase in current density arising from restriction of the surface of the larger electrode.

Local corrosion of iron sometimes arises from the trapping of air bubbles in slight hollows already existing, and the oxidation and deepening of these spots by successive portions of entrapped air. Pitting, however, from localised causes other than those arising from the nature of the metal, is not common in boilers, because any liquid or gaseous corrosive substance introduced into the boiler tends to be diffused over all the exposed surface by the agitation and circulation of the water and atmosphere in the boiler.

The external corrosion of a boiler shell differs in no essential respect from the corrosion of other structural iron, which has been already dealt with in the first chapter of this section.

The same protective effect that is obtained by "galvanising" iron is sometimes secured for a boiler by hanging zinc plates or spheres in the water, with the object of diverting attack thereto and saving the boiler plates; the action is a galvanic one in which the zinc is the attacked plate. The theory on which the use of zinc for this purpose is based is sound, but it is essential that good metallic contact be maintained between the zinc and the boiler plate, a condition which is not easily obtained in ordinary boiler practice. The quality of the zinc is also important. It should preferably be rolled and not cast, as the crystals in a cast plate have been found to separate with a black insulating medium between them; and it should also be pure, as if it contains lead this may be deposited as the zinc dissolves, and set up the very action it is intended to prevent. Metallic aluminium is also used for the same purpose.

Another protective agent has recently been suggested as a remedy for the electrolytic corrosion of boilers. It has been found that solutions of chromic acid and its salts inhibit the rusting of iron by rendering the surface of the metal "passive" in some way. Many explanations have been offered for this effect, but it is not yet completely understood.

In view of the important part which oxygen plays in the corrosion of boilers, it seems reasonable to believe that if no oxygen be allowed to reach the iron through the water no corrosion

can take place. The removal of dissolved oxygen or air from boiler waters has, indeed, been proposed, the pre-heating of the water, and the use of scrap iron, being among the methods which have been suggested for this purpose.

SOFTENING AND PURIFICATION OF BOILER WATER.—After a water intended for use in a boiler has been analysed and its mineral constituents determined, it is possible to pronounce whether it can be used in its natural state, and, if not, what treatment it must first undergo. In considering water purification it is convenient to divide the impurities which need removal into two classes—namely, those which are precipitated on boiling the water under atmospheric pressure, and those which are not deposited under such conditions. In the first class calcium carbonate is the commonest impurity; the behaviour of magnesium carbonate is similar but not identical, as its deposition from boiling water is less complete than that of calcium carbonate. A saturated solution of calcium carbonate in water saturated with CO_2 at 10° C. = 50° F. and 760 mm., contains 61·6 grains per gallon of this salt, and one of magnesium carbonate under like circumstances contains 2,030 grains per gallon. On boiling such solutions at atmospheric pressure, the bulk of each salt is precipitated, the amount left in solution being about 2·5 grains per gallon for calcium carbonate, and 7 grains per gallon for magnesium carbonate. In actual boiler waters such a condition of saturation does not occur, but the quantities of $CaCO_3$ and $MgCO_3$ left in solution when the water is boiled at atmospheric pressure, are approximately those just given, although some allowance must be made for the solvent influence of other salts simultaneously present. It is evident from this that the bulk of these carbonates can be removed by boiling the water previous to its admission to the boiler; this is practised when feed water is heated by waste steam, a deposit being then produced in the heater instead of in the boiler.*

The same action occurs in reservoirs used to store water at a high temperature and pressure outside the boiler—in order to meet emergency demands, as in the case of boilers at electric lighting stations—with the addition that $CaSO_4$ is also thrown down. In many cases, as in non-condensing engines utilising the exhaust steam for producing a furnace draught, pre-heating the feed water is impracticable, and the removal of $CaCO_3$ and $MgCO_3$ must be otherwise effected.

The process usually adopted consists in adding lime to the

* Mere heating under atmospheric pressure only frees the water from $MgCO_3$ and $CaCO_3$, and leaves untouched the still more objectionable scale-forming constituent, $CaSO_4$ (*v.i.*).

water to be softened, in amount just sufficient to combine with that quantity of CO_2 which is concerned in holding the $CaCO_3$ and $MgCO_3$ in solution, whether it exist as bicarbonate or in the free state. If the CO_2 were present in the proportion indicated by the formula $CaCO_3, H_2CO_3$ (the calcium bicarbonate sometimes assumed to exist, see p. 132), the quantity of lime requisite would be equivalent to the lime and magnesia present as carbonates in the water. Such relation between the carbonates and the CO_2 is not found in natural waters, there being always an excess of CO_2, necessitating a larger amount of lime to effect the softening than that which corresponds with the $CaCO_3$ and $MgCO_3$ present. The function of the lime is to combine with the CO_2 other than that present as $CaCO_3$ and $MgCO_3$ to form $CaCO_3$; this is precipitated, and, simultaneously, pre-existing $CaCO_3$ and $MgCO_3$ are also precipitated.

It has been found by E. Bartow and J. M. Lindgren that in the treatment of waters containing bicarbonates of lime, soda, and magnesia with lime water, the reactions proceed in regular order, the lime acting successively on the CO_2 combined with the lime, soda, and magnesia. If, therefore, insufficient lime is added to the water, calcium carbonate will be precipitated in preference to magnesium carbonate.

In practice, where space permits, the lime is best added in the form of lime water, made by stirring excess of lime with water until saturation is effected, and allowing the undissolved lime to settle; the clear liquid contains about 80 to 90 grains of CaO per gallon, and is more reliable in its action than milk of lime, inasmuch as its composition is always known, whereas milk of lime may vary largely in content of CaO. Where space is limited, and a separate tank for the preparation of lime water cannot be used, a weighed quantity of lime, sufficient for treating a known volume of water, is stirred into a cream with a little water, and added to the contents of the tank in which the softening is to be carried out. To ascertain whether an excess of lime has accidentally been added (such excess being objectionable, as it causes formation of incrustation in a boiler), some test which will show whether calcium hydroxide is present in solution, must be applied to a small filtered portion of the water. Tests commonly in use for this purpose consist in the precipitation of silver oxide from the nitrate, of mercuric oxide from mercuric chloride, or in observing the reaction with phenolphthalein. With waters containing magnesium salts, such as the chloride, the first effect of lime in excess of that necessary to combine with the CO_2 is to decompose these magnesium salts, and a portion of the resulting magnesium hydroxide remains in solution until the water is

heated, when it is deposited, frequently on the injectors and other feeding apparatus of the boiler. This drawback is met by Archbutt by passing furnace gases into the treated water, the CO_2 thus introduced serving to carbonate any excess of lime or any magnesia that may be present, with at most, the effect of producing a slight scale in the boiler. The proper amount of lime, either in solution or as a cream, having been added, and thoroughly mixed with the water, separation of the precipitate can be effected either by subsidence or filtration. The former is the simpler, the latter the more rapid method, and choice between them depends on local circumstances. This process of lime treatment was originated by Clark, improvements in filtration having been added by Porter, whence the term "Porter-Clark process," as applied to precipitation by lime and filtration through filter presses. It will be understood that this process is only adapted for removing that portion of the incrustation-forming constituents which is precipitated when the water is boiled under atmospheric pressure, and that it is without action on others—*e.g.*, $CaSO_4$; moreover, a certain amount of $CaCO_3$ and $MgCO_3$, corresponding with the solubility of these substances, remains in solution. With these limitations the process is efficacious in dealing with many hard calcareous waters.

When ferrous carbonate is present in a water, this will also be precipitated on treatment with lime; mere aëration will also suffice to remove it, since it oxidises, yielding ferric hydroxide or basic carbonate, which is insoluble in water. The precipitate should be separated by subsidence, as it causes the oxidation of the cloth of the filter press, acting as a carrier of oxygen from the air to the fibre.

Since the water in the boiler is used at a temperature above 100° C., often attaining, in high-pressure boilers, 150° to 200° C. = 302° to 392° F., it is not sufficient to treat the water so as to remove merely those substances which are precipitated on boiling under atmospheric pressure, particularly as these substances are not the worst offenders in the formation of scale. Calcium sulphate is the most objectionable constituent of a boiler water of the hard calcareous class, since it forms with the $CaCO_3$, which is generally simultaneously present, a particularly dense and adherent scale, the reason for the deposition of which has been already dealt with at p. 132. The usual method of treating waters containing $CaSO_4$ consists in the addition of sodium carbonate, which forms calcium carbonate and sodium sulphate by double decomposition with the $CaSO_4$. When the water also contains $CaCO_3$ and $MgCO_3$, it may be first freed therefrom by addition of lime, and then further purified from $CaSO_4$

by Na_2CO_3. The softening agents can be added together, when they become, in effect, a mixture of caustic soda and calcium carbonate (when equivalent quantities are used), or these substances together with an excess of either original reagent (when the quantities do not happen to be equivalent). Caustic soda alone can be used when the amount of CO_2 to be saturated is precisely equivalent to the quantity of calcium sulphate to be precipitated by the resulting sodium carbonate. When this relation does not obtain, the caustic soda must be supplemented by lime, should the CO_2 be present in greater amount than that equivalent to the $CaSO_4$ contained in the water, but by sodium carbonate should the amount of CO_2 be smaller than this equivalent. The following equations will make these relations clear :—

$$(1)\ CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$
$$(2)\ Na_2CO_3 + CaSO_4 = Na_2SO_4 + CaCO_3.$$

If the sodium carbonate produced according to the first equation be more than sufficient to precipitate the whole of the $CaSO_4$ in accordance with the second equation, a portion will remain in solution, and both constitute a waste and be injurious from a steam-raising point of view. On the other hand, if the CO_2 in the first equation be insufficient to produce enough sodium carbonate for the realisation of the second equation, the whole of the $CaSO_4$ will not be precipitated, and the water will still yield an incrustation. Save in so far as it allows of the use of a more compact form of softening agent, the use of caustic soda is less to be commended than that of lime and sodium carbonate in the correct proportions, except where filter presses are to be used, and the total precipitate to be handled must be kept at a minimum.

All the well-known patented forms of water softening apparatus are based on the above chemical reactions. The methods of regulating and proportioning the supply of reagents have been brought much nearer perfection than formerly. They differ from one another simply in the mechanical arrangement of the plant, and in the devices for rendering the apparatus automatic in its action.

An attempt has been made to substitute magnesia for caustic soda as a precipitating agent, the method consisting in filtering the water through sawdust mixed with MgO. The first effect is to precipitate $CaCO_3$ and $MgCO_3$ by saturation of the CO_2 which keeps them in solution, the resulting magnesium carbonate from both sources then reacting with the $CaSO_4$, forming $MgSO_4$ and $CaCO_3$; a certain amount of $MgCO_3$ remains in solution, but its

deposition on the boiler is not greatly objectionable, as the sludge formed is loose and non-adherent. The presence of magnesium salts in solution, however, makes the formation of magnesium chloride and its subsequent decomposition in the boiler probable, and is, so far, undesirable. Other methods—chiefly of chemical rather than of technical interest, on account of the high cost of the materials—for treating boiler water containing $CaSO_4$ are those involving the use of barium compounds, including the chloride, hydroxide, and carbonate, and of various sodium salts, particularly the phosphate, fluoride, and aluminate. Barium chloride decomposes the $CaSO_4$ by double decomposition, yielding $CaCl_2$ and $BaSO_4$, which latter, however, settles slowly. Barium hydroxide and carbonate act in a similar manner, the latter forming two insoluble compounds by reacting with the calcium sulphate—viz., $CaCO_3$ and $BaSO_4$.

Sodium phosphate has been used to some extent as an alternative to sodium carbonate; it reacts with $CaSO_4$, forming calcium phosphate. The advantages claimed for it are its convenience of application, and the fact that the precipitate formed is flocculent and non-adhesive, whilst that prdouced by Na_2CO_3 is somewhat dense and crystalline. Its use is limited by reason of its high price and its high combining weight, which make it nine times as costly as Na_2CO_3; moreover, it cannot be used cold, the reaction being slow and incomplete without the application of heat.

Sodium fluoride is not used to any extent; it gives calcium fluoride, a somewhat voluminous precipitate, sodium sulphate remaining in solution.

Sodium aluminate acts like caustic soda, with the addition that the precipitate of aluminium hydroxide which is formed at the same time acts as a coagulant. It precipitates the bicarbonates of lime and magnesia, and also reacts with other magnesium salts. Calcium sulphate, however, is unaffected by it.

Attempts have been made to deposit all the incrusting substances which are present in the feed water, in the boiler itself, not allowing the deposit to be distributed generally over the surface of the boiler, but confining the deposition to spots accessible for cleaning out. Of this type is an apparatus consisting of a delivery tube for the feed water, passing through the water space of the boiler, and having its exit end above the water level. $CaCO_3$, $CaSO_4$, etc., are deposited in this feed pipe before the water debouches into the boiler itself, and can be mechanically removed. The success of devices of this class chiefly depends on allowing the feed water to travel slowly to its exit, so as to allow time for complete deposition. It must be understood that the

trouble of incrustation is not removed, but transferred from the boiler to the feeding apparatus.

Various plans have been suggested for overcoming the sluggish subsidence of the precipitate obtained when certain waters are softened, notably those drawn from a river instead of a well, and containing organic and clayey matter in suspension. A simple and efficacious plan consists in leaving the sludge from the first purification in the precipitating tanks in which the next batch of water is to be treated, and agitating this sludge with the water *during treatment.* The coarse preformed precipitate induces the deposition of the freshly-formed, finely-divided precipitate. A small quantity of alum, aluminium sulphate, or ferrous sulphate is sometimes added together with the lime; the flocculent hydroxide of aluminium or iron thus precipitated entangles the suspended matter and hastens clarification.

The evils attending the presence of oil and grease in boiler feed waters have already been commented upon, and it is important that methods for removing this objectionable impurity should be adopted. Exhaust steam separators afford a partial solution of the problem. In these contrivances the steam is treated as such, and a partial condensation allowed to take place. The resulting water washes the remaining steam, the oily water being separated either continuously or at intervals. These contrivances, however, are not absolutely effective.

Filtration through sand or sponges has been employed more or less successfully, but the most satisfactory method of eliminating oil is by chemical means. This entails the formation of a precipitate uniformly throughout the water by the introduction of chemicals. The precipitate absorbs or clings to the oily particles, and both are removed together by filtration. The precipitate may be either $CaCO_3$, $Mg(OH)_2$, $Al(OH)_3$, $Fe(OH)_3$, or a mixture of several of these. One cheap method often used for removing oil from condenser water is to pass it first through a sand filter, and then add it to the ordinary boiler feed supply and pass it through the softening plant. The $CaCO_3$ precipitated in the latter carries down with it all the remaining oily or greasy particles.

A reagent very largely employed in this way for removing oil and suspended matters generally, known as "alumino-ferric," is crude aluminium sulphate. A precipitate of aluminium hydroxide, $Al_2(OH)_6$, is prepared by the interaction, *in situ*, of this salt, and some alkali, such as Na_2CO_3, NaOH, or lime water.

e.g., $Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Al_2(OH)_6 + 3Na_2SO_4 + 3CO_2$.

Still another method has been recently adopted for removing

oil from water by means of electrolysis. *A continuous current of electricity is passed through the water while it is passing between electrodes of aluminium or iron.* The electrodes are gradually consumed, and a precipitate of aluminium or iron hydroxide is formed which collects the oil particles in the manner described above. The current has also a separate distinct effect upon the oil which tends to hasten the coalescence of the small globules into larger ones. In general, the resistance of condenser water is too high to permit of the passage of a sufficient current, and it is necessary to add hard water, or some suitable salt, to get over this difficulty.

It must not be supposed that a water when free from constituents capable of forming an incrustation is necessarily suitable for boiler use. If hard with calcium sulphate, the removal of this substance by means of sodium carbonate leaves in solution an equivalent of sodium sulphate, which, if present in large quantity, is found to cause "priming" in the boiler. (By the *term* **priming** *is meant such tumultuous ebullition as causes the* projection of finely-divided water, as spray, into the steam space, whence *it travels to the cylinder, causing bad economy* in the working of the engine.) Excess of sodium carbonate added to the water has the same effect, and natural waters containing sodium carbonate (which are not uncommon) of course act similarly. Such waters may even have to be treated with calcium chloride to decompose the sodium carbonate and leave the comparatively harmless sodium chloride.

Although a considerable amount of work has been done on the subject of priming, it is still very obscure. M'Gill draws the following practical conclusions from his investigations on the subject:—

(1) The contents of sodium salts must be kept down to a minimum. Marked foaming takes place under 10 lbs. pressure *when the contents of* Na_2O reach 1,500 *parts per million* (105 grs. per gall.). At 200 lbs. pressure it is presumable that the foaming *limit will be at a much lower concentration.*

(2) Calcium hydrate in excess will cause foaming in presence of saponifiable fats, which are always present, in traces, in boiler concentrates. Hence the necessity of avoiding excess of lime in water treatment. This applies still more strongly to sodium hydrate.

(3) Solid matter in suspension predisposes to foaming.

In connection with this subject is a very singular point, to which attention has been given lately, and which is now well established; it is that under boiler conditions Na_2CO_3 may become to some extent converted into NaOH. The exact way

in which this occurs is still uncertain. Among those who have investigated the question may be mentioned Messrs. Tatlock & Thomson, of Glasgow, who, "from a consideration of the whole question, think it possible that the $Mg(OH)_2$ produced from the $MgCO_3$ acts slowly as a causticising agent at the high temperature inside the boiler." In one case in which 1,000 gallons were concentrated to 20 gallons, 15 per cent. of the total Na_2CO_3 was converted to NaOH.

Boiler Compositions.—To avoid the cost of the plant necessary for removing the scale-forming constituents in a feed water, it is customary, especially on the part of small power users, to add some composition to the water in the boiler with a view of preventing the deposition of a coherent incrustation. Many proprietary preparations are sold for this purpose, of which it is sufficient to say that none should be used without a knowledge both of its composition and of that of the water to be treated, and that all are sold at prices bearing but a remote relation to their intrinsic values.

Caustic soda or soda ash (Na_2CO_3) forms the basis of a very large number of these **anti-incrustators**; these are effective when used in the proportion demanded by the particular water to be treated, but may cause priming if added in excess. They owe their virtue to the fact that they decompose calcium carbonate and sulphate, with the result that the deposition of calcium sulphate is avoided and the incrustation is comparatively loose. The prevention of a dense adherent scale being the object of the use of these preparations, any salt capable of forming a non-cohering precipitate with the calcium sulphate in a hard water may be employed, provided it has no objectionable action of its own; for example, sodium phosphate and barium chloride are constituents occasionally adopted. The decomposition of calcium carbonate in the boiler is sometimes achieved by preparations containing ammonium chloride, which forms calcium chloride and ammonium carbonate; the latter substance is deleterious, since it is volatile and exercises a corrosive action on copper and its alloys forming parts or fittings of the boiler. The use of ammonium chloride for this purpose has now been almost abandoned.

Other anti-incrustators which have for their object the formation of a loose sludge in place of a coherent scale, are efficient to some extent in that they contain amorphous organic rubbish—peat, sawdust, etc.—which hinders the mutual adherence of the scale-forming constituents of a boiler water. A similar result is arrived at by employing tannin and other vegetable extractive matters; in this case the action is aided by the formation of the

lime salts of slightly acid substances of the character of tannic acid. The following analysis by Tatlock represents a typical anti-incrustator :—

NaOH	12·30	per cent.
Na_2CO_3	1·24	,,
Na_2SO_4	0·68	,,
$CaCO_3$	0·48	,,
Tannin	6·65	,,
Organic matter	19·60	,,
Water	59·05	,,
	100·0	

Still another class of anti-incrustator has for its object that of increasing the solubility of the incrusting salts, and thus prevent their precipitation. The most usual of these substances are gelatine, sugar, and molasses.

A very common practice in America, and on the State Railways of Austria, Hungary, and Belgium, is to put petroleum into the boilers to prevent scale. Its action is purely mechanical. It gives an infinitesimal coating of oil to the crystals, which prevents them from cohering. Its effect is not lasting, as the petroleum is gradually volatilised. Only refined petroleum (kerosene) is used, as the crude oil is liable to give a dangerous greasy deposit. An objection to fatty substances, which have also been exploited, has been already stated under the head of *oily incrustations* (p. 141). Anti-incrustators have their value under certain conditions of limited space or smallness of plant, but if adopted they should be bought under their own names and at their own market prices, instead of at fancy rates under proprietary titles.

CHAPTER IV.

THE CHEMISTRY OF LUBRICANTS AND LUBRICATION.

The function of a lubricant being to keep the surfaces on which it is smeared from coming into contact with each other, and at the same time to allow of their motion relative to each other to take place with as little impediment as possible, it is obvious that a special class of bodies must be used for these purposes, having particles which slide easily over each other, while having sufficient cohesion to prevent the ready rupture of a film composed of them.

A further result of this conception of the functions of a lubricant is the realisation of the fact that the speed with which the surfaces move over each other, and the pressure tending to force them together, must be considered in choosing any individual from the class fitted for a given kind of work. The logical outcome of this is that every different kind of bearing needs a different lubricant to enable it to run with the least friction. In practice it suffices to use a different kind of lubricant for each different class of bearing, even when the members of the class are not identical. The disadvantages of using a lubricant not the absolutely best for the bearing, is more than compensated for by the advantage of having comparatively few kinds of lubricants to provide and distribute.

Oils may be regarded as typical lubricants. Fatty oils, that is to say, oils consisting of the glyceryl salts of acids of the fatty and similar series, have been almost exclusively used until comparatively modern times. Since the rise of the petroleum industry it has been found that certain of the fractions obtained in distilling crude petroleum, which are intermediate between the light burning oils and the heavy pitchy residue, are excellent lubricants, possessing important properties which give them, in some respects, the preference over fatty oils; they are, accordingly, largely prepared and used. Of solid lubricants there is a considerable variety, the individual members of which are chiefly used where exceptionally heavy loads are to be carried, or where,

as in outdoor use, a cheap lubricant that will not drain or be washed away, is wanted. Such are axle grease, cart grease, black lead, tallow, and soapstone compositions.

FATTY OILS.—For a fatty oil to be of use as a lubricant it is essential that it should be non-drying (see *Oils*, Vol. II.). It is also desirable that it should not readily become rancid, as during the change understood by the phrase "becoming rancid," free fatty acids are often produced, which have a corrosive action on metallic surfaces with which they are in contact. The soaps of the heavy metals thus formed are pasty substances of too sticky a nature to be serviceable as lubricants. Oils which fulfil these conditions are sperm oil, neatsfoot oil, lard oil, castor oil, and, in smaller degree, olive oil, tallow, and rape oil. The first four are specially free from tendency either to dry or to become rancid, and are, therefore, the best examples of their class. Choice between them depends on their viscosity or "body," sperm oil being a light oil of low viscosity, which, however, it retains as the temperature rises, whilst neatsfoot oil and lard oil are of greater viscosity, but diminish in body with rise of temperature to a greater extent than does sperm oil. Castor oil is distinguished by its great viscosity, on which account it is used for lubricating heavily loaded journals. With regard to the remaining three, olive oil is a good lubricant if originally free from fatty acid, and not allowed to become rancid in use; rape oil is also useful on account of its high viscosity, the advantage of which compensates in great measure for the drawback arising from its tendency to gum. Tallow is esteemed for heavy loads and high temperatures, and is, therefore, used for cylinder lubrication, but is apt to be decomposed by high-pressure steam, and consequently to yield fatty acids and their salts of iron, copper, by action upon metals with which it is in contact.

In stating the viscosity of an oil, it is usual to adopt the viscosity of rape oil at 60° F. as a standard and to call it 100. The oils described above have at 60° F. = 15·5° C. viscosities which, referred to this standard, are represented by the following figures:—

Sperm oil,	32
Neatsfoot oil,	87
Lard oil,	88
Castor oil,	1,100
Olive oil,	72
Rape oil,	100

The difference in drop of viscosity with rise in temperature in oils of this class is shown in the following table:—

Oil.	Viscosity at		
	15·5° C. = 60° F.	50° C. = 122° F.	100° C. = 212° F.
Sperm oil,	32	19	15
Olive ,,	72	24	16
Rape ,,	100	30	17
Castor ,,	1,100	157	27

These figures indicate the class of work for which each of the foregoing oils is most suitable, it being a general rule that for quick-running bearings, carrying low pressures, an oil of low viscosity is best fitted, whilst for heavy pressures an oil of higher viscosity is required. Furthermore, where a bearing is liable to rise in temperature during use, it is desirable that the oil employed for lubricating it should change as little as possible in *viscosity with rise of temperature. In selecting an oil its* viscosity must be considered as regards the temperature which is likely to prevail during the running of the bearing; at temperatures above and below this the oil will not be working to the best advantage, but such imperfection is of little practical moment, if the viscosity be adapted for the mean temperature of the bearing.

The behaviour of a lubricating oil at low temperatures is also of obvious importance. As a rule, an oil is required to remain liquid at the temperature at which it is to be employed. On exposure to cold an oil generally assumes the consistency of a jelly or ointment, and refuses to flow freely. The determination of the temperature at which the oil undergoes this change is known as the "*cold test*," and it should not be inconsistent with the conditions under which it is to be used. In lubricating oils to be used in railroad practice, the cold test is a vital one, and receives considerable attention. On American railways, for instance, it is not uncommon to specify that paraffin and neutral oils shall have a cold test above 10° F. for winter and 32° F. for summer use. Lubricating oils from Russian petroleum bear exposure to a very low temperature (— 20° F.) without becoming solidified. For the lubrication of air-driven rock drills, where low temperatures are experienced, kerosene has been successfully used.

The classes of bearings which may be lubricated economically by the oils spoken of above, are indicated in the following synopsis :—

Sperm oil, . Quick running spindles lightly loaded.
Neatsfoot oil, . Bearings exposed to low temperatures and mechanism in which risk of corrosion is specially to be avoided (*v.i.*)—*e.g., clocks.*

Lard oil, . . Shafting, engine, and machinery bearings.
Castor oil, . Bearings working at heavy pressures and high speed.
Olive oil, . . Moderate pressure and high speed.
Rape oil, . . Engine bearings and cylinder lubrication.*
Tallow, . . Cylinder lubrication.*

All fatty oils in their condition as expressed or rendered, contain free fatty acid, varying in amount from about 1 per cent. in the case of good sperm oil, to 10 per cent. for common olive oil (calculated as oleic acid). It is a sound general principle that lubricating oils should contain the least possible quantity of free fatty acid; 4 per cent. (calculated as oleic acid) is the maximum permissible. Oils that are refined by treatment with sulphuric acid—*e.g.*, rape oil—are liable to contain traces of this acid, either free or in the form of a sulphonic acid. This impurity is highly objectionable for lubrication.

It must be remembered that all fatty oils tend to develop free fatty acids on keeping and in use (see *Oils*, Vol. II.), and that on this account a sample originally nearly free from free fatty acid may become acid to an objectionable extent during use. Olive oil is the worst, in this respect, of those mentioned above. As the temperature rises, the tendency for the development of free fatty acid increases, and when the oil is also in contact with high-pressure steam, hydrolysis occurs freely and much fatty acid is liberated.

The general character of the fatty lubricating oils is given in the section on fats and oils.

MINERAL OILS.—These are all higher fractions of petroleum and shale oil, and are produced in many different grades, ranging from a light oil as thin as sperm to a semi-solid mass resembling axle grease in consistency. The exact grade to be used in any given case is determined by consideration of the load to be carried and the speed of the journal; the higher the speed and the lighter the load, the thinner the oil that will give the best results. The following table gives the viscosity of oils at different temperatures suitable for distinct classes of bearings, the viscosity of rape oil at 60° F. = 15·5° C., being taken as 100:—

	60° F. = 15·5° C.	140° F. = 60° C.	180° F. = 82° C.	220° F. = 104° C.
Cylinder, . . .	*Semi-solid*	30	17	12
Medium machinery, .	100	19	13	10
Spindle, . . .	53	9	5	3

* No fatty oil is really suitable for cylinder lubrication.

When once the best oil has been decided upon, future supplies of satisfactory quality can be obtained by comparing the results of a chemical examination of the two samples, and seeing that the essential properties of the oil, and notably the viscosities at different temperatures, are substantially identical. The fault of most mineral oil is the great loss of viscosity which they undergo by rise of temperature (as will be seen from the above table), so that an oil which at the ordinary temperature of the air is amply viscous for its purpose, may become altogether too fluid and mobile at the temperature of the bearing which it is used to lubricate. Russian mineral oils lose their viscosity with an increase in temperature more rapidly than do American oils of the same specific gravity, but in both classes the reduction is most rapid in the case of the most viscous oils, and as the Russian have a higher viscosity than American oils a more rapid reduction in the former case might be anticipated. The viscosity of an oil should, therefore, be determined at the maximum temperature that the class of bearing upon which it is to be employed is likely to attain. Besides a suitable viscosity, mineral oils used for lubrication should have a high flashing point, considerably above the maximum temperature to which they are likely to be exposed. Seeing that mineral oils are obtained by processes of fractional distillation, they frequently contain constituents of lower boiling point than that at which the main part of the oil begins to distil, and consequently may possess a low flashing point (see *Petroleum*, Vol. II.). For a lubricant, a low flashing point is injurious, as it involves a greater fire risk, and also occasions waste by evaporation during use. This objection does not arise with fatty oils, for their flashing points are usually high—*e.g.*, 400° to 500° F. = 204° to 260° C. No mineral oil should be used as a lubricant which has a lower flashing point than 150° C. = 302° F.; and when high temperatures have to be provided for, as in cylinder lubrication, still higher flashing points—*e.g.*, 200° to 250° C. = 392° to 482° F.—are requisite. In the foregoing figures the **flashing point** meant is that obtained by the "close test;"* when the "open test" (identical with the close test, save that the vessel in which it is performed is freely open to the air) is adopted, flashing points from 30° to 60° F. higher than those given by the close test are obtained for the same class of oil. The temperature at which the oil remains ignited (**firing point**) is still higher, the difference being sometimes as much as 100° F. The statement of the flashing point of an oil should, therefore,

* This is carried out by heating the oil in a vessel which allows of very limited access of air, and applying a light as the temperature rises, until the vapour from the oil ignites with a slight flash.

always be accompanied by a note of the method by which it has been determined.

In a cylinder oil, besides the necessity for a high flashing point, is the requirement that the oil should yield but little matter volatile in a current of steam, lest a portion of it be vaporised with the exhaust steam, and, entering the condenser, find its way into the boiler (p. 141). As it may happen that a portion of the oil is volatile independently of the presence of steam, this quality should also be determined in valuing a mineral oil. The loss at the maximum temperature to which the oil is to be exposed, should not exceed 1 per cent. in six hours. A good mineral lubricating oil should be thoroughly refined—that is, free from mineral or organic acid, alkali, and tarry matter. Paraffin wax should be absent, as it separates on cooling, forming a semi-solid magma instead of a highly viscous fluid.

MIXED OILS.—The facts that mineral oils have no tendency to change by exposure to the air, and neither gum nor attack the metal of the bearings, and that fatty oils retain their viscosity fairly well on rise of temperature, have led to the use of mixed oils, which to some extent combine the good qualities of both classes. As, however, they are invariably sold under fancy names, at fancy prices, it is always cheaper and more satisfactory for the user of lubricants, should he need sufficiently large quantities, to buy fatty and mineral oils separately, under proper expert advice, regard being had to the class of bearing to be lubricated; such oils may then be blended by himself. Prominent among mixed oils are cylinder oils and "valvolines," which are intended to carry the heavy pressures and endure the high temperatures that obtain inside a steam cylinder. Heavy fatty lubricants, such as tallow, are apt not only to lose a great proportion of their viscosity at these temperatures, but are also split up by the steam in the manner already referred to, and the liberated fatty acids act freely on the metal of the cylinder with which they are in contact, producing masses consisting of the soaps of the heavy metals. These soaps not only block and gum up the moving parts, but are indications of the fact that, to produce them, serious corrosion must have occurred. Very heavy semi-solid mineral oils mixed with fatty oils or with soaps are, therefore, found to lead to less trouble than fats alone, the corrosion being greatly less, while sufficient viscosity to properly lubricate the moving surfaces is retained. Most fatty oils can be used for improving mineral oils in respect of constancy of viscosity, and even those which become rancid and hydrolyse readily are less liable to those changes when in a mixture, than when used *per se*—the mineral oil exercising a protective influence.

Seeing that the function of the fatty oil added to a mineral lubricant is to raise its viscosity, castor oil is frequently used for this purpose; it is, however, not miscible in all proportions with mineral oil, and its blending is, therefore, effected by the addition of a third oil, such as lard or rape oil. Blown oils, which are prepared from rape or cotton seed oil (see *Oils*, Vol. II.), have a viscosity even surpassing that of castor oil, but their use is not legitimate unless acknowledged.

The use of mineral oils, sometimes of very indifferent quality, or ill-fitted for the purpose to which they are applied, has led to attempts to increase their viscosity, especially at high temperature, by the addition of various substances, which may be conveniently known generically as **oil thickeners.**

Mineral oils may be rendered solid or semi-solid by the addition to them of a small quantity of soap—that is, the alkali salt of a fatty acid. The "soaps" containing other metals, notably aluminium, combined with a fatty acid, are still more effective. There is a considerable trade in the manufacture of aluminium oleate, stearate, and palmitate, which are generally prepared by precipitating the corresponding sodium salt with alum or aluminium sulphate.

A mixture of mineral oil with 10 per cent. of aluminium soap has been sold largely under the misleading name, "gelatin." Opinions differ as to the efficacy of such oil thickeners. The spurious viscosity is said to rapidly diminish when the oil is heated. Some authorities regard this addition to mineral oils as pure adulteration. On the one hand, it has been objected that in contact with water and steam the aluminium soap is precipitated and clogs the machinery, while, on the other hand, it is maintained that by the presence of aluminium soap the adherence of the lubricant to metal surfaces is much increased.

These bodies (**oil pulp**) are dissolved in a small quantity of mineral oil and the product (**oil thickener**) used for the purpose above-named, by addition (in regulated amount) to the oil it is desired to thicken. Unless acknowledged and offered to the consumer without disguise, oils thus thickened must be considered adulterated. Indiarubber, rosin, and similar viscous materials are also employed for the same purpose.

Analysis of such an oil thickener is quoted by Allen:—

		Per cent.
Mineral oil (specific gravity 0·906),		48
Lard oil,		15
Alumina,	Oil pulp.	6
Fatty acids,	Oil pulp.	30

To remedy the defect which some liquid lubricants have, of

being wasteful in use, and to reduce their consumption, a class of oils known as "**cohesion oils**" have been compounded, which are distinguished by a lower degree of fluidity than the ordinary grades. Opinions vary as to the efficiency of these oils. The basis of them is a more or less viscous fat; crude rape oil is most frequently used, whilst occasionally tallow, palm oil, neat's foot oil, or other solid fat is added to reduce the fluidity. In addition, they all contain resin oil (8 to 20 per cent.) and American pine resin, which imparts the characteristic property of viscosity. A typical analysis of such an oil is—

	Per cent.
Raw rape oil.	76
Refined tallow, ...	4
Resin oil, ...	10
American pine resin, ...	10
	100

A product known as "*soluble petroleum*" is prepared by partially saponifying resin previously dissolved in the oil, or by blowing air through a mixture of rosin oil and caustic soda solution, and adding to the jelly-like mass thus obtained an aqueous solution of a fatty oil soap, and mineral lubricating oil. The product is intended to be employed in admixture with water, as a lubricant, especially for tools used in boring and cutting metals, and is stated to have given excellent results. It should be remembered that lubricants for cutting tools not only reduce friction between the chip and the tool, but when used in sufficient quantities help to dissipate the heat generated, and thus increase the life and output of the tool. Lard and sperm oils are very good lubricants for cutting wrought iron and steel, whilst a 5 per cent. solution of sodium carbonate is also excellent. Another lubricant commonly used is an aqueous solution of soft soap and soda.

A further example of the compounding of mixed oils may be seen in the following table showing the composition of three **turbine-oils** suitable for light, quick-running shafts, and axles:—

	1.	2.	3.
	Per cent.	Per cent.	Per cent.
Yellow resin oil, ...	75	28	40
Blue "	12·5	..	..
Olive oil, ...	..	28	..
Rape oil, ...	12·5	..	..
Olein, ...	..	44	..
Cottonseed oil, ...	..	..	30
Paraffin oil, ...	..	..	30

For the purpose of disguising the presence of mineral oils, certain compounds are sometimes added to destroy their fluorescence or "bloom." This peculiar property may sometimes be obscured by exposure to light, but more rapidly and certainly by subjecting the oil to a process of limited oxidation by treatment with nitric acid. Turmeric, α-nitronaphthalene, picric acid, and dinitrotoluene also destroy the fluorescence, the last named being frequently used in the proportion of 4 lbs. to the ton of oil.

SOLID LUBRICANTS.—Tallow by itself cannot be considered as a good example of a solid lubricant, as when used alone it is generally for cylinders where the temperature is above its melting point, and it functions merely as an ordinary oil. A better instance of a solid lubricant is afforded by the mixture of tallow and plumbago sometimes used for heavily loaded journals where the temperature is low enough to allow of the tallow retaining its condition of solidity.

The following analyses represent some typical tallow lubricants. Nos. 1 and 2 are said to be used on the Austrian railways in summer and winter respectively, while No. 3 is a very efficient axle grease frequently used in Belgium and England :—

	1.	2.		3.
	Per cent.	Per cent.		Per cent.
Tallow,	90	75	Tallow,	64
Olive oil,	1	15	Pork fat,	16
Pork or horse fat,	9	10	Palm oil,	16
			Graphite,	4

Probably the largest use for solid lubricants is for railway carriage axles. Good axle grease consists of a small quantity of soap serving to entangle, render more concrete and thoroughly emulsify a mixture of fat or fatty oil and water. The usual procedure in making these greases is to mix tallow or palm oil, or both, with a liquid fatty oil—such as rape oil—water, and caustic soda or carbonate of soda, the alkali serving to form a small quantity of soap with the fatty acid invariably present in commercial oils and fats, and to act in the manner described above. It needs much skill to procure a good grease of which the constituents will not segregate on exposure to the temperature which it is likely to attain when used as a lubricant—*e.g.*, 150° F. = 65° C. As the fats of which the grease is made melt at a temperature below that which the grease is intended to endure, the amount of soap and water emulsified by means of

the soap, are the chief causes of its satisfying this condition, and it is perfectly possible, therefore, to prepare a grease which is both more costly and less effective than another properly mixed.

Reducing the amount of water very much below 40 per cent. is apt to cause the fat to segregate when the grease is heated, and the grease to fuse as a whole at a temperature below that normal to a grease of good quality. On the other hand, increasing the water much above 50 per cent. robs the grease of some of its lubricating power, and is, moreover, unless provided for by a lower price, a fraud. For common purposes, especially for outdoor work, such as the greasing of trolly axles, rosin grease is used. It consists of rosin oil (see *Destructive distillation*, Vol. II.) treated with slaked lime, which converts it into a pasty mass of fair lubricating qualities. Rosin oil is composed of a number of unsaturated hydrocarbons, some of which have the property of combining with the hydroxides of the alkalies and alkaline earths; the resin acids generally present in rosin oil doubtless contribute to this result. The compound thus formed can emulsify a large excess of rosin oil, so that commercial rosin grease may contain over 96 per cent. of its weight of rosin oil. Barium sulphate, kaolin, calcium carbonate, and black lead are often added as make-weights, and, if gritty, are not only diluents, but also actively objectionable. Soapstone would be a more reasonable addition. The following percentage composition is that of a typical railway grease:—Water 50, tallow 30, palm oil 10, sodium carbonate 10.

It has been already mentioned that mineral oils may be rendered solid or semi-solid by the addition to them of soap. Such "solid petroleum lubricants" are largely used as axle greases, and they are usually prepared by saponifying a fat by means of lime, soda, or occasionally litharge, and dissolving the resulting soap in mineral oil. The following analyses represent typical axle greases belonging to this class (*Archbutt*):—

Lime Soap Grease.		Soda Soap Grease.		Lead Soap Grease.	
Mineral oil (0·885-0·912),	72·0	Mineral oil,	55·00	Mineral oil,	48·0
Neutral oil or fat,	0·5	Neutral fat,	8·97	Neutral fat,	8·7
Fatty anhydride,	17·6	Soda soap,	16·11	Fatty acid,	2·6
Lime,	1·9	Sodium carbonate,	3·19	Resin acid,	9·9
Water,	8·0	Sodium sulphate,	1·67	Lead oxide,	3·0
		Water,	15·06	Lime,	0·9
				Water,	27·2
	100·0		100·00		100·3

Vaseline and crude lanolin ("wool fat") are also used for lubricating purposes, and are said to form excellent axle greases.

Such a grease may be prepared by heating some vegetable oil with milk of lime and vaseline and then adding melted lanolin. The following figures indicate approximately the proportions of ingredients used :—

Crude vaseline,	100	The grease may be stiffened by the addition of 10 to 20 per cent. of soapstone.
Crude lanolin,	8	
Rape oil,	2	
Quicklime,	1	
Water,	4	

The use of graphite, either alone or mixed with various oils and greases, as a lubricant, has extended so largely in recent years that it deserves separate mention. It is not easily carried away from the wearing surfaces, can stand great pressure, and requires only an infinitesimal clearance-space between surfaces by filling up all the minute cavities and irregularities in the surfaces, giving a hard polished surface which requires relatively little lubricant. It is, moreover, peculiarly fitted as a lubricant for gas-engine cylinders, being entirely inert and unaffected by heat or cold, steam or acids.

A modified form of graphite known as "colloidal" or "deflocculated" graphite has been introduced recently by Acheson. In this form the graphite is in an extremely fine state of division, and is suspended either in oil or water, according to the conditions under which it is to be used.

CORROSION INDUCED BY LUBRICANTS.—Corrosion is induced by the presence of free fatty acids in fatty oils and in admixtures of these with mineral oils; it increases, though perhaps not in direct ratio, with the percentage of free fatty acid. Oils, whether fatty or mineral, imperfectly refined and containing in consequence free mineral acid, or sulphonates which are readily split up into acid products, will also give rise to corrosion.

It seems probable from Donath's experiments that the corrosive action on metals of lubricating oils containing free fatty acids depends to a great extent on whether the oiled surfaces come into contact with atmospheric oxygen, and whether, by condensation, or other means, water gets into the oil. It is difficult to account in any other way for the very erratic manner in which corrosion sometimes takes place.

It is an interesting fact that the soaps of iron and other heavy metals are soluble in hydrocarbons, though insoluble in water, the reverse being the case with the alkali soaps. Consequently the iron soaps produced in cylinders by fatty oils become dissolved out whenever a change to mineral oil is made. This fact is well

known, but it has been wrongly attributed to a production of gummy matter by the mineral oil itself.

"Brass" bearings—that is, bearings made of gun-metal or similar alloys—are often severely attacked by an acid lubricant, while iron and steel are less affected, and white metal bearings suffer least of all. A lubricant containing an appreciable amount (over 4 per cent.) of free acid before being put into use, should not be tolerated. Those containing fatty oils may, although originally neutral, develop fatty acid (p. 157), and their conditions of use may be such that this alteration is inevitable. The development of acidity in oils is of considerable importance in *modern engineering practice*, inasmuch as most large users of lubricants arrange to supply a continuous stream of oil to all heavily loaded bearings that must be kept cool, and recover the oil, filter it, and use it again. Mere filtration will not affect its acidity, and if of a nature to become acid, it should be freed from acid at intervals by treatment with caustic soda, or rejected altogether, and a new supply procured after due analysis.

PART II.

METALLURGY.

METALLURGY deals with the treatment of metalliferous minerals (ores) for the purpose of winning the metals which they contain, and with the subsequent purification of the crude metal first obtained. For convenience, metallurgical processes may be regarded as falling into two classes, dry and wet, the former including those in which advantage is taken of the reactions which occur at high temperatures, and the latter dealing with those dependent on such reactions as take place in aqueous solution.

A. **METALLIFEROUS ORES.**—Comparatively few of the metals are found native—*i.e.*, in the metallic state—either approximately pure or alloyed with some cognate metal; the majority of them occur in the form of true ores, which are compounds of metals with non-metallic elements. The following classification includes most of the common ores :—

(1) As metals—Copper, bismuth, mercury, silver, gold, platinum and its congeners. Silver and gold are found alloyed.
(2) As oxides—Iron, copper, tin, zinc, manganese and aluminium.
(3) As sulphides—Lead, copper, zinc, antimony and mercury.
(4) As carbonates—Copper, zinc, lead and iron.
(5) As haloid salts—Silver, aluminium and sodium.
(6) As arsenides and antimonides—Nickel * and cobalt.

It must not be supposed that commercial ores are usually pure substances of fixed composition, like those to which they are referred in the foregoing list. Pure specimeus of each of the compounds exist, but are too rare to form a source of the metal. The ease with which metals replace each other in minerals, leads to the existence of ores which, although referable to oue of the above classes, contain two or more metals. Thus, unmixed sulphides of copper are far less common than copper pyrites, which contains both sulphide of copper and that of iron. Ores

* Also found in large quantities as a double silicate of nickel and magnesium.

are associated with valueless earthy matters—*e.g.*, oxides, carbonates, and silicates of difficultly reducible metals, such as aluminium, calcium, and magnesium (also with silica as quartz). *The necessity for the separation of this* **gangue** *before the mineral* can be profitably reduced to metal, much diminishes the value of the ore.

B. **METALLURGICAL PROCESSES.—DRESSING (Sizing** and **Concentration).**—This consists in partially freeing the ore from gangue by mechanical methods, and comprises hand-picking, to remove large lumps, followed by reduction to coarse powder and separation by **levigation.** The first crushing of large pieces of ore is usually performed by some modified form of Blake's jaw-crusher. The impure ore is then taken either to crushing rollers or to the stamping-mill. Sizing apparatus or sorting machines are employed for dividing the crushed ore-stuff into grains of several sizes. One kind of apparatus in use consists of a series of flat-bottomed sieves with graduated meshes placed on different levels and mechanically agitated. Rotating drum-sieves or trommels are, however, more frequently employed. After the ore stuff has been thus sorted according to the size of the grains, the next step is to separate by specific gravity or otherwise the pure ore from the gangue associated with it. If more than one kind of mineral is present these are also frequently separated by gravity. For this purpose hydraulic or pneumatic jiggers are employed, in which the particles are washed by a stream of water (or air), whilst being subjected to repeated up and down motion, in which the ascent of the jigging stuff takes place by jerks, but in the descent it falls freely. In this way the ore collects at the bottom, and the gangue is skimmed off or otherwise removed from the surface. For dressing fine sandy, mealy, or slimy ore-stuff, buddles or sloping tables are used, over which the fine stuff suspended in water descends, the particles of different specific gravity being deposited in different parts of the "table." There is an endless variety of these jiggers and buddles, for details of which the larger works on metallurgy should be consulted. For an illustration of mechanical dressing, the treatment of tin ore, which will be dealt with in its own section, may be quoted. Where the ore is magnetic, it is possible to separate it from the gangue by washing the crushed ore between the poles of a magnet.

The applications of magnetism to ore dressiug have received considerable attention in recent years, and fall undel two heads—

(1) Concentration of magnetic minerals from the gangue.

(2) Separation of two or more minerals of similar specific gravity in the products of a preliminary water treatment.

Magnetic concentration (as distinct from magnetic separation) finds its principal use in the treatment of magnetic iron ores (*q.v.*). Ores carrying chalcopyrite (copper pyrites, $CuFeS_2$) are also treated in this way. This mineral has a tendency to slime when crushed, which gives rise to important losses in subsequent wet concentration: by roasting it becomes magnetic, and is readily saved by magnetic attraction, even if finely divided. Minor applications are in the separation of leucite ($Al_2O_3 . K_2O . 4SiO_2$) from lava, and in the treatment of garnetiferous schists.

The operations of **magnetic separation** are generally more complex. As is well known, all substances are acted upon by a magnetic field, though in very different degrees. In modern magnetic separating machines advantage is taken of *small* differences which various minerals exhibit in their behaviour in a magnetic field. The method has proved of great importance for separating zinc blende from pyrite, marcasite, or siderite (ferrous carbonate). These latter minerals are almost non-magnetic, but can be made magnetic by roastiug and subsequently separated from the non-magnetic zinc mineral. Oxidised zinc ores often occur associated with hydrated oxide of iron (limonite), a slightly magnetic mineral which may be separated in a highly intense magnetic field, or rendered more strongly magnetic by roasting, and then removed. Magnetic separation also finds application in the treatment of magnetic sand, in separating tin-tungsten concentrates, and in the purification of corundum (Al_2O_3). (See also under *Iron*, p. 179, and *Tin*, p. 297.)

In a more recent type of apparatus static electricity is employed instead of magnetism. Advantage is taken of the differences of repulsion exerted by or upon the electrically charged particles of metalliferous and non-metalliferous material respectively. Practically all sulphides except zinc blende are conductors of electricity, and thus a separation of blende from pyrite may be made, which is not possible in the wet way. Copper minerals are, as a rule, conductors of electricity; the silicates and carbonates least so, while the compounds with sulphur, arsenic, and antimony are very good conductors. In such a process various difficulties have to be overcome, connected more especially with insulation, feeding, and dust. The size of the particles must be within certain limits, and it can easily be understood that the presence of dust is harmful, since a non-conducting particle may be converted into a condncting particle by being covered with the dust of a conducting mineral. Climatic conditions also affect the success of the operation. In spite of these difficulties, however, there seems to be a field for electrostatic separation

in arid regions, where water for milling purposes is scarce. The method has made great advances in recent years. Materials which are good conductors passing over a surface highly charged with electricity are rapidly charged with like electricity, and are consequently repelled, while poor conductors are slowly affected, and drop nearly perpendicularly from the field. The separation may be made sharper by passing the concentrated material over a surface charged with the opposite electricity when the charge in the good conducting material is reversed, and the material is rapidly repelled, while poor conductors, being charged with opposite electricity, are attracted to the electrode surface.

The last few years have witnessed the development of a number of new processes of ore concentration entirely different in principle from any of the foregoing, and in which the results of simple jigging are reversed, the concentrates being removed from the top, and the tailings or gangue from the bottom. They may be roughly grouped under the head of "**Flotation Processes,**" although this title is not always scientifically justified. These methods depend mainly on the property of "differential surface tension"—*i.e.*, on a difference in the adhesive power of various liquids (and gases) to the surfaces of different minerals. No single satisfactory explanation which will cover all the observed phenomena can be given, and the adaptability of a flotation process to any particular ore can be determined only by experiment.

It seems probable that the surface tension between water and minerals, such as quartz and silicates, is greater than that between water and metallic minerals. A simple flotation method for treating sulphide ores is based on this principle alone. In this process the carefully sized particles of ore are projected in a particular manner on to the surface of water in such a way that the sulphide particles float on the surface, while the particles of gangue sink. These sulphide particles are supposed to have a peculiar superficial property or "greasy" character, which prevents them becoming wetted and penetrating the water surface, while rock constituents do not possess this property, and easily break through the surface and sink.

It is found that these differences are emphasised if the material to be treated is mixed with oil, the adhesion of which to sulphides and gangue material is the reverse of that shown by water. Moreover, oil being lighter than water is itself an active agent of flotation, and, in addition, serves to agglomerate the sulphide particles. If gas be generated from the minerals by the addition of acid to the tank in which the ore is being treated, the small rising bubbles selectively attach themselves to the particles of metallic sulphide, and float them to the surface, where they are

drawn off as a metallic scum, the gangue settling to the bottom. Among the means used to accelerate the process and effect a more perfect separation are deepening the tanks, heating the liquid, and partially exhausting the air above the liquid in the tank. The forces employed in ore flotation are most delicately balanced, and in any given case the process to be worked will require adjustment to the character of the ore by careful experiment.

EXTRACTION.—Both wet and dry methods of extraction are in use, the former being the more recent and in many cases more rational; speaking generally, however, wet processes have not been brought to such comparative efficiency as the dry methods, which have the advantage of centuries of experience in their working. The only essential process common to wet methods is the leaching out of the metal by means of a suitable solvent. To render this possible, some preliminary treatment is frequently necessary, to convert the metal into a soluble salt; for example, the treatment of silver ores by the Augustin process (*q.v.*). The subsequent extraction of the metal from the solution is specific for each case, and no general principles can be laid down. In dry processes, however, certain general methods can be distinguished—viz., roasting (calcination), reduction, and refining.

Roasting and Calcination.—The object of these processes is generally the elimination of sulphur, arsenic, carbon dioxide, or bituminous matter from the ore, as well as to render it more porous and suitable for subsequent smelting. In the case of sulphur and arsenic, these are removed in roasting by oxidation, SO_2 and As_4O_6 being volatile. Carbon dioxide is simply removed in calcination by the dissociation of the carbonate containing it; bituminous matter is also burnt away during the process, itself serving as the fuel. The operation is sometimes still conducted in heaps which consist partly of the fuel and partly of the ore; sometimes in stalls, which are rectangular spaces enclosed on three sides by brick walls and open at the front and top, the former being closed by a temporary wall after the introduction of the charge. More generally, some form of reverberatory furnace is used, as the roaster; muffles—*e.g.*, for blende—may be used, and various contrivances for continuous roasting, which will be spoken of individually. The product is usually a more or less pure oxide of the metal.

Occasionally the object of roasting is to form, not an oxide, but a chloride, sulphide, or arsenide. Common salt is the usual chloridising agent, and is mixed with carbon and the ore before roasting, while iron or copper pyrites, barium or calcium sulphates, and metallic sulphides are common sulphurising agents. Nickel and cobalt behave with regard to arsenic as silver and

copper do in the case of sulphur. These metals may be protected from the scorifying action of silicates by means of their affinity for arsenic. Such an artificial arsenide is called a "speiss" and a sulphide a "regulus."

Reduction (including fluxing).—By reduction is meant the obtainment of the metal as such from the ore. Since the preliminary roasting has converted the ore into an oxide, the subsequent reduction consists in removing the oxygen by hot carbon or carbon monoxide. In order that the separated metal may agglomerate, it is frequently necessary to render fluid residual gangue by the addition of some **flux**—*i.e.*, a substance capable of forming a fusible slag with the said gangue. The nature of this flux depends on that of the gangue, and is either "acid" (*e.g.*, SiO_2) or "basic" (*e.g.*, CaO), according as the gangue is basic or acid. Reduction is generally effected by the direct action of carbonaceous fuel, or by means of carbon monoxide in a reverberatory furnace. Occasionally, however, the metallurgist makes use of other reducing agents, such as iron, manganese, lead, aluminium, or sulphides. For instance, lead and antimony are obtained by the reduction of their sulphides by iron at high temperatures, when iron sulphide is formed and the metals liberated. The use of aluminium as a reducing agent is seen in Goldschmidt's process, in which metallic oxides or sulphides are reduced by firing a mixture of them with aluminium powder—*e.g.*,

$$Cr_2O_3 + 2Al = Al_2O_3 + Cr_2$$
$$3CuS + 2Al = Al_2S_3 + 3Cu.$$

There is, however, a certain class of ores which is capable of "self-reduction"—*i.e.*, of requiring the introduction of no extraneous reducing agent. In such ores the sulphur occurring as sulphide in one portion may be used to remove the oxygen existing as oxide from another portion, the metal from each being thus freed. Ignoring secondary reactions, the following equation will represent a case of this kind :—

$$2PbO + PbS = 3Pb + SO_2.$$

Refining.—This term is applied to the removal of impurities from the crude metal obtained by reduction. Refining by oxidation generally consists in partially oxidising the metal by roasting in a current of air, whereby the more readily oxidised impurities are oxidised and either volatilised or removed as slag. Examples of this are the refining of crude copper and the puddling and bessemerising of iron. A variation consists in using some of the oxide of the metal as the oxidising agent, instead of, or supplementary to, air. When this process is adopted, it is frequently

necessary to correct the refined metal, which itself has become slightly oxidised, by a secondary reduction process; the "poling" of copper serves as an example. Metallic oxides, such as manganese peroxide, are frequently useful in the oxidation of impurities in metals. Ferrous oxide or silicate, too, may act as a carrier of oxygen, and serve to oxidise impurities in the following way:—When a molten slag containing ferrous silicate is exposed to the air partial oxidation takes place, and crystals of magnetic oxide are formed. Such a slag, in contact with impure metal, gives up its excess of oxygen from the magnetic oxide to the oxidisable elements present, and again becomes reduced to ferrous oxide. Potassium and sodium nitrates are also used as oxidising agents in refining silver and antimony. This process is not applicable to the removal of impurities less oxidisable than the metal to be refined—*e.g.*, silver from copper. Refining by **liquation** depends upon the difference between the melting point of the metal to be purified and those of its impurities. The metal is exposed to a temperature just sufficient to melt it and to cause it to flow away from the less fusible impurities. Thus, crude tin is eliquated from its impurities, such as iron and copper. Another general principle of which advantage is taken in refining, is that involving the use of immiscible solvents. This process, which consists in extracting a substance dissolved in one liquid by means of another liquid in which the substance is more soluble, the two liquids being immiscible (for a parallel case the extraction of iodine from its aqueous solution by means of carbon disulphide may be quoted), is exemplified by the Parkes process of desilverising lead. The argentiferous lead is fused and treated with zinc, which is nearly insoluble in lead, and is at the same time a better solvent for silver than is lead. The zinc, containing silver, floats on the surface, and is skimmed off. A similar method is that of "settling out," in which one metal is allowed to subside, by reason of its higher specific gravity, from another in which it is immiscible, the two layers being then separated.

Another process of obtaining fairly refined metals, and that directly from the ore, consists in distilling the ore, if necessary previously roasted to oxide, with carbon. Mercury, cadmium, and zinc are thus obtained. With the increased use of the extremely high temperatures attainable by the electric furnace, it is not improbable that this method may be extended to the winning of metals less volatile than these three.

Yet another process, not only of refining metals, but of obtaining metals directly, is of sufficient importance to deserve separate mention—viz., the electrolytic method. This is employed in both the wet and dry way, a fused bath forming the electrolyte

in the latter modification of the process. Electrolysis is mainly employed in the refining of copper, silver, gold, and nickel, and for the production of aluminium, nickel, and several of the rarer metals, such as calcium. Pure iron is also now being obtained by electrolysis.

One other method may be noted, in which the metal is extracted *from its ores by means of a reagent which acts as a "carrier"* of the metal. After the separation of the metal the "carrier" is again available for the treatment of a further quantity of ore. Such a process is typified by Mond's process for extracting nickel in which carbon monoxide is the reagent employed.

IRON.

Although iron is one of the most widely diffused elements, it is only sufficiently abundant in certain distinct ores to be worth working. The characteristic red, brown, or yellow colour of ferric oxide in the anhydrous or hydrated state, proclaims the presence of iron in many soils and rocks, when the actual quantity contained therein is relatively inconsiderable. Thus, reddish sandstones and sands containing iron oxide are common enough, but the proportion of iron is far too small to render it profitable to remove the siliceous impurity which forms the bulk of the material.

The term iron ore strictly includes only those minerals which contain iron, not only in sufficient quantity, but also in a condition which enables them to be employed for the economic production of the metal. To be of value iron ores must be rich, pure, plentiful, and easily reduced. It is found in practice that *only the oxides and carbonates fulfil these conditions.*

Native iron (iron in the metallic state) occurs too rarely to be of any commercial importance. Some meteorites are chiefly composed of iron, as may be seen from the following typical *example*:—

	Per cent.
Iron,	90·88
Nickel,	8·45
Cobalt,	0·66
	99·99

Globules of metallic iron have been found in basalt and other igneous rocks, and occasionally fused masses of iron are found in coal measures.

ORES.—Oxides of Iron.—The most important of these are the ores known as hæmatites from the fact that certain varieties

have a blood-red colour. Two classes are distinguished, the first, red hæmatites, are anhydrous ferric oxide, the others, brown hæmatites, being hydrated.

The former contain up to 70 per cent. of iron (this being the percentage in pure Fe_2O_3). They are usually associated with earthy matters, so that this percentage is reduced to 60 to 65 per cent. Red hæmatite proper is known as **kidney ore** from the shape of the pieces in which it is found; it has a fibrous structure, a dull red colour, and specific gravity about 5·0. It is a common form in Cumberland.

Specular Iron Ore, a crystalline variety, is so called on account of its mirror-like lustre; it is dark grey, but when powdered is red. Both these forms are widely distributed in the United Kingdom. There are also notable deposits of hæmatite at Bilboa in Spain and in the United States, whilst specular iron ore occurs in the Island of Elba, in Brazil, Canada, and Central India. On account of its freedom from impurities this ore yields a cast iron which is especially well adapted for the production of wrought iron and steel.

Micaceous iron ore is a pure variety of the anhydrous oxide occurring in large quantities in North America. It derives its name from the glistening dark grey scales which resemble mica.

The brown hæmatites (**limonite**) contain, when pure, $2Fe_2O_3 . 3H_2O$, which corresponds with a content of 60 per cent. of iron, though the ores actually worked rarely contain much more than 50 per cent. Northamptonshire and Spain are the chief sources of brown hæmatite for iron making in this country. The brown hæmatite deposits of Luxemburg-Lorraine are among the most important in Europe, and form the chief source of iron in Germany and France. This supply of ore is said to be larger than that in any other country. The ore closely resembles that of Northamptonshire, but varies considerably in composition. The ores which are worked contain from 40 to 60 per cent. of Fe_2O_3 and 10 per cent. of water. They are also phosphoric, containing 0·5 to 2·0 per cent. of phosphorus, and their use has increased enormously since the introduction of the basic process (*q.v.*). Brown hæmatites are valuable because they can be easily mined, and are readily reduced in the blast furnace.

The **laterites** of India are a group of porous argillaceous tertiary rocks containing a considerable quantity of brown hydrated iron oxide. The richer kinds are employed to a small extent as a source of iron. A special variety of industrial importance is **bog-iron ore** used for the purification of gas (see *Destructive distillation*, Vol. II.). The following analyses give the composition of typical red and brown hæmatites:—

	Red Hæmatite.	Brown Hæmatite.	Northampton Limonite
	Per cent.	Per cent.	Per cent.
Fe_2O_3,*	90·36	80·80	65·00
MnO,	0·10	1·13	0·50
Al_2O_3,	0·37	..	3·50
CaO,	0·71	2·48	2·50
MgO,	0·06	..	..
P_2O_5,	Trace	..	1·30
FeS_2,	0·06	..	..
Insoluble siliceous residue,	8·54	5·55	13·20
Water and volatile matter,	..	8·98	14·00
	100·20	98·94	100·00
* Corresponding with metallic iron,	63·25	56·56	45·50

The only other oxide of iron of importance as an ore, is the **magnetic oxide** (*magnetite*), the typical formula of which is $FeO . Fe_2O_3$, although the proportion of FeO to Fe_2O_3 may vary from the ratio 1 : 1 (which corresponds with 72·5 per cent. of metallic iron). The proportion of the iron is, however, generally considerably smaller than is indicated by this formula, from the presence of siliceous and earthy matter, as is shown by the following analyses :—

	1. Dannemora.	2.	3. Swedish Magnetite.
	Per cent.	Per cent.	Per cent.
Fe_2O_3, *	62·06	44·40	59·00
FeO, *	28·42	20·00	28·00
MnO,	..	0·16	0·10
CaO,	Trace	0·60	0·40
MgO,	1·44	1·00	0·10
Al_2O_3,	Trace	5·20	0·30
P_2O_5,	..	0·50	0·03
Sulphur,	0·07	Trace	..
Insoluble siliceous matter,	7·60	24·20	12·00
Water,	..	2·50	..
	99·59	98·56	99·93
* Corresponding with metallic iron,	65·60	46·63	63·08

This ore is met with in immense quantities in Sweden (from which the celebrated Swedish iron is obtained), in the Lake Superior district of North America, and in the Madras Presidency in India. The magnetites and hæmatites of the Lake Superior

district now constitute the largest supply of iron ore in the world. Impure varieties of magnetite also occur in which either the ferrous or ferric oxide is replaced by the oxide of another metal. The most important of these are (1) **franklinite** or **zincite,** and (2) **ilmenite** or **titanic iron ore.** The former occurs in New Jersey, and contains oxides of zinc and manganese. In modern practice franklinite is separated from other zinc minerals by a magnetic concentrator, and then used for the production of oxide of zinc and spiegel-eisen. **Ilmenite** occurs in the massive form in Norway, and as magnetic sands in the United States, Canada, and New Zealand. It is usually considered to be a mixture of ferrous titanate, $FeO \cdot TiO_2$, and ferric oxide, but is more probably an isomorphous mixture of the sesquioxides of iron and titanium, and best represented by the formula $(FeTi)\,O_3$. It is difficult to smelt in the blast furnace, owing to the formation of the curious cyano-nitride of titanium, $Ti(CN)_2 + 3Ti_3N_2$, and the somewhat infusible slags which are formed. According to the Report of the Canadian Commission (1907), however, there is no insurmountable difficulty in smelting this refractory ore in an electric furnace, a pig iron containing only 0·40 per cent. Ti being produced from iron sands containing as much as 17·0 per cent. of TiO_2.

Carbonate of Iron (*Spathic Iron Ore*).—The pure mineral is ferrous carbonate, $FeCO_3$, and contains 48·2 per cent. of Fe; it is usually associated, however, with carbonates of manganese, lime, and magnesia. It is not very abundant in the United Kingdom, the chief localities being in Durham and Somersetshire; on the Continent it is more abundant, notably in Styria. Its freedom from phosphorus makes it suitable for the manufacture of certain classes of steel. The following analyses exhibit its composition:—

	Somersetshire.	Styria.
	Per cent.	Per cent.
FeO, *	43·84	55·64
Fe_2O_3,	0·81	...
MnO, †	12·64	2·80
CaO,	0·28	0·92
MgO,	3·63	1·77
CO_2,	38·86	38·35
H_2O,	0·18	...
Insoluble matter,	0·08	...
	100·32	99·48
* Corresponding with metallic iron,	34·67	43·27
† Corresponding with metallic manganese,	9·80	2·17

Clay ironstone is ferrous carbonate associated with clay and sand. It is the most abundant English ore, and occurs in the *coalfields of Wales, the Midlands, and Scotland. A variety of* clay ironstone is **black-band** ore, which contains much carbonaceous matter, whence its name. The celebrated Cleveland ore is a clay ironstone which is poor in manganese, but rather richer in phosphorus than are most other ores of this class. Clay ironstones are also found in strata containing coal, limestone, and fireclay: all these materials are required in iron manufacture.

The following are analyses of clay ironstones:—

	Scotch Blackband.	Clay Ironstone.	
		Low Moor.	Cleveland.
FeO } *	41·0	36·14	39·92
Fe_2O_3, }	2·5	1·45	3·60
MnO,	1·0	1·38	0·95
Al_2O_3,	3·0	6·74	7·86
CaO,	2·0	2·70	7·44
MgO,	1·0	2·17	3·82
Alkalies,	..	0·65	0·27
CO_2,	26·0	26·57	22·85
FeS_2,	..	0·10	0·11
P_2O_5,	0·5	0·34	1·86
SiO_2,	7·0	17·37	7·12
Water,	1·0	1·77	2·97
Organic matter,	15·0	2·40	1·64
	100·0	99·78	100·41
* *Corresponding with metallic iron,*	33·6	29·13	33·62

Sulphide of Iron.—Iron pyrites, FeS_2, is never directly smelted, *but spent pyrites from vitriol making (q.v., Vol. II.) is occasionally* used as a source of iron.

PRINCIPLES OF IRON EXTRACTION.—Where a pure oxide of iron is attainable, a malleable (approximately pure) iron can be prepared by direct reduction with charcoal. This is still practised where charcoal is cheap, and pure magnetite, etc., abundant. This reduction is probably effected according to the equation:—

$$Fe_3O_4 + 4CO = Fe_3 + 4CO_2.$$

The pure iron thus reduced, although infusible at ordinary *furnace temperatures, is obtained in a partly agglomerated state,* the particles not being separated by foreign siliceous matter. In the case of an ordinary ore containing argillaceous or siliceous

matter, such agglomeration does not take place unless the clay, etc., be fluxed by the addition of limestone, which forms fusible silicates—slag—therewith. The scarcity of charcoal in this country necessitates the use of a fuel with a high content of ash (viz., coke): the presence of this ash, which is siliceous, also demands a basic flux. The impurities in the ore and fuel introduce sulphur, phosphorus, and silicon into the iron, and a portion of the carbon of the fuel is also taken up, the resulting crude iron being more fusible than the pure metal, and, therefore, running together as a liquid instead of agglomerating as a paste—a condition which renders continuous working practicable. The application of these principles will be dealt with under appropriate headings.

PREPARATION OF THE ORE FOR SMELTING.—Ores which contain shale or pyrites (FeS_2) in objectionable quantities are sometimes stacked in heaps and exposed to the action of the weather for some months. The separation of shale by hand-picking is often a matter of great difficulty, but by the process of "weathering" it gradually crumbles to powder. In this way, too, pyrites is oxidised to ferrous sulphate ($FeSO_4$), together with free sulphuric acid, and is washed out by the drainage water. Calcareous ores containing pyrites should not be weathered, for in this case calcium sulphate is formed, a substance which is nearly, if not quite, as objectionable as the original pyrites. In order to expose as large a surface to the reducing gases of the blast furnace (*v.i.*) as is compatible with the free passage of the blast between the fragments of ore, the ore is crushed, in most cases to about 2-inch cubes. The crushing is effected by ordinary stone-breakers, or by crushing rolls.

It is not usually profitable to apply any system of concentration to iron ores other than magnetites, and in certain cases hæmatites. The removal of gangue by hand-picking is occasionally practised, and various mechanical concentrators are used to some extent for washing iron ores, more especially in the United States. A more important method is that of **magnetic separation,** which consists essentially in sizing the ore by means of sieves, and passing it between the poles of powerful electro-magnets, which retain magnetic oxide, and allow free passage for the gangue. According to Prof. W. A. Anthony ("Magnetic Concentration of Ores," *Cassier's Magazine*, 1898, xiii., p. 433), electro-magnetic separators may be divided into classes:—

(*a*) Those in which the mixed material is carried round or in front of the poles of a magnet, and in which the magnetic portion is deflected from its course sufficiently to be deposited in a receptacle by itself.

(*b*) Those in which the material spread out upon a carrier *passes in front of a magnet, which picks up the magnetic portion*, which is then, either by the magnet itself, or by means of a supplementary carrier, removed to a separate receptacle. The "Monarch" and the "Wetherill" machines are representatives of these two classes respectively.

Magnetic concentration is used principally for magnetites, but hæmatite ores may also be treated in this way, after first calcining them with a small proportion (1 to 5 per cent.) of coal, whereby the ferric oxide is reduced to the intermediate stage of oxidation, and thus rendered magnetic.

This process of concentration not only removes a considerable proportion of the gangue, but it has the additional advantage of eliminating a large proportion of the phosphorus, and in some cases also the sulphur present in the ore. Practically this is the *only method of removing phosphorus from ores* which has been successful on a large scale: it is also stated that pyrites is more readily removed by magnetic concentrators than by calcination.

Most iron ores, save those which are free from volatile constituents—*e.g.*, magnetites and red hæmatites (unless they contain pyrites)—are roasted before being reduced. This is done either in open heaps, which consist of a pile of ore and small coal (except in the case of blackband, which contains its own fuel), or in rectangular enclosures, the walls of which are 6 to 12 feet in height. The combustion of the heap is started by brushwood. Various kilns, heated by solid fuel or producer gas, or in some cases by the waste gas of the blast furnace, are also used for roasting. Gaseous fuel has been particularly successful with pyritic ores in Sweden and America, it being found that sulphur is much more perfectly removed in this way than when coal is used. The advantages of kilns over open heaps are that the former occupy comparatively little space, are continuous in action, and can be placed near the blast furnace. Moreover, the consumption of fuel is less than in open working, and the ore being protected from the weather, the process is much more under control.

The advantages of roasting are—(1) the expulsion of volatile constituents—*e.g.*, water, CO_2, sulphur, and arsenic—and *pari passu* the concentration of the ore and of the waste gases from the blast furnace (*v.i.*); (2) the rendering of the ore more porous, and consequently more permeable by the reducing gases of the blast furnace; and (3) the oxidation of Fe'', which forms a stronger base than Fe''', and, therefore, tends to pass into the slag as silicate.

REDUCTION OF THE ORE IN BLAST FURNACES.—The modern blast furnace is a masonry tower, A (Fig. 14), 75 to

90 feet high, lined with firebrick, the interior of which is so built that it is of the form of the frustra of two cones base to base. It is encased in an outer shell constructed of wrought iron or mild steel plates, ½ inch thick, riveted together; the upper frustrum, B, constituting about three-fourths of the total height, is called the **stack** or **body.** It is supported on a cast-iron ring resting on pillars of the same material. The lower frustrum, C, is termed the **boshes,** and is also cased with iron, while water cooling boxes, made of gun-metal, are frequently inserted in the

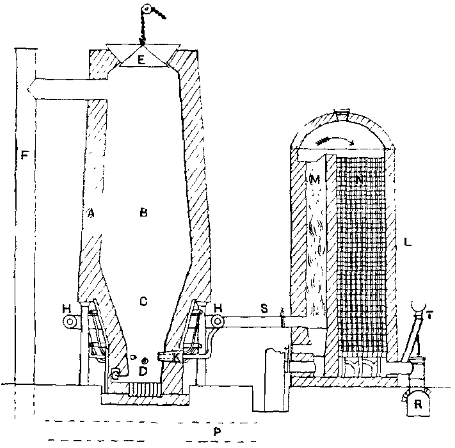


Fig. 14.—Blast furnace.

A, Masonry tower; B, body; C, boshes; D, hearth or crucible; E, cup and cone for closing throat; F, exit pipe; G, tapping hole; H, air-supply pipe; K, twyers; L, Cowper stove; M, flue; N, chequer firebrick; P, underground pipe; R, flue to chimney; S, T, air pipes leading to twyers.

lining. The diameter across the boshes (the **belly**) is about 24 feet. The lowest portion of all, D, is the **hearth** or **crucible,** and is about 8 feet in diameter. It is independent of the masonry

of the stack, being built in after the latter is completed. The upper end, or **throat,** of the furnace, about 16 feet in diameter, is closed by a cast-iron cup and cone, E, to allow of charging without interfering with the exit of the gases through the pipe, F. At the bottom of the hearth a space, G, is left in the brickwork, which can be tamped up while the fused metal is collecting, and unstopped when the charge is ready to be drawn. To avoid the fluxing action of the slag, the firebrick lining of the boshes is sometimes replaced by bricks of graphite coke, which are, however, liable to wear and tear by oxidation. On account of the high temperature needed for the smelting of iron, large volumes of air at a considerable pressure have to be supplied to induce sufficiently rapid combustion; it is obvious that, within certain limits, it is advantageous to heat the blast. For instance, the use of a hot blast will effect a saving of 15 to 45 per cent. of fuel. The air is supplied from a blowing engine, through the pipe, H, which nearly surrounds the boshes, and is provided with a number of jets, K, called the **tuyeres (twyers),** which pass into the furnace at the upper part of the hearth. The nozzles of the twyers are protected from the heat of the hearth by a jacket through which cold water is circulated. The air supply is heated by passage through the **Cowper** or **Whitwell stove,** L, or some modification, such as the Massick and Crookes, or Ford and Moncur, or Cowper-Kennedy. All these act on the regenerative principle (*q.v.*), and serve to heat the blast. The Cowper stove consists of a tower containing a flue, M, the remainder being filled with chequer firebrick, N. The object of this stove is to utilise the heat of the gases from the blast furnace, as well as that produced by the combustion of the CO, etc., contained in them. Their value as a fuel may be judged from the following analyses, which are typical of gases obtained when coke and coal are used as fuel, though in actual practice considerable variations occur (*Turner*):—

	Fuel Used.	
	Coke.	Bituminous Coal.
	Per cent.	Per cent.
CO,	25	28·0
CO_2,	12	8·6
N,	59	53·5
H,	2	5·5
CH_4,	2	4·4

Great developments are being made in the direct use of blast furnace gases, after purifying, for producing power in gas engines.

The gases from the blast furnace (at a temperature of about 250° C. = 482° F.) pass by an underground pipe, P, into the flue of the stove, where they meet a supply of air and are burnt, the products of combustion travelling down through the chequer brickwork, N, to which they impart their sensible heat, before passing away to the chimney by R. The waste gases sometimes contain an objectionable amount of dust, which clogs up the hot blast stoves; moreover, the dust may itself be of value (as when it contains zinc). For these reasons it is the custom to insert some form of "dust-catcher" in the "down-comer" or wide pipe bringing the waste gases from the furnace to the stoves. In one form of dust-catcher now in general use the gases pass down a central tube at a relatively high speed, and enter a much wider tube, up which they rise with a much smaller velocity, after which they pass to the main gas flue. The dust collects in the bottom of the wide tube, and is periodically removed. These stoves are worked in sets, one being heated in the manner described above, while another is serving to heat the air blast, which is forced in the contrary direction through the pipes, S, T, to the twyers. The pipe thus serves to feed all the stoves. Formerly the blast was heated by passage through cast-iron pipes, set in a furnace fed by the combustible gases from the blast furnace—a method which allowed of continuous working with a single stove—but the need of higher temperatures made cast iron an unsuitable material for the construction of the stove, and simple substitution of a fireclay for a cast-iron tube was impracticable, owing to the difficulty of keeping it tight to the pressure of the blast (2½ to 7 lbs. per square inch), and a plan whereby the air was heated by direct contact with a mass of refractory material had to be adopted. A modern hot blast has a temperature of about 800° C. = 1,472° F. Where blast furnaces are worked with raw coal instead of coke, the condensable products of the destructive distillation of the fuel (notably tar and ammonia, the latter in the proportion of 0·1 to 0·15 per cent. of the waste gases) are collected before the gas is burnt in the stoves. This is effected either by passing the gases through an air condenser and water scrubber, similar to those used in gas manufacture (*q.v.*, Vol. II.), or by treating the gases with a shower of sulphuric acid, both methods involving the cooling of large volumes of gas. To avoid this it has been proposed to mix the blast-furnace gases with SO_2 from pyrites kilns, and to collect the resulting ammonium sulphite. In consequence of certain

defects, due to incomplete condensation and contamination of the ammonium sulphate with tar, these acid processes are not now employed. By the first-mentioned method (a recent modification of which is the Gillespie process, in which improved washers of a special type are used) about 40 gallons of crude tar and 24 lbs. of ammonium sulphate per ton of coal are obtained.

A recent development in blast-furnace practice is the drying of the air before passing it through the stoves. This is accomplished by drawing the air through refrigerators in which the moisture is condensed. The heat which would have to be expended in raising the temperature of the water vapour to that of the exit gases from the stoves is thereby saved. Moreover, by thus drying the air it is claimed to be possible to increase the burden of the furnace, and production of pig iron by 20 per cent., to reduce the amount of coke per ton by 18 per cent., and to diminish the duty on the blowing engines, the effective capacity of which, in terms of oxygen, is greater on account of the colder air being more dense. The greatest advantage, however, is in the increased regularity of working the furnace, particularly where marked variations in temperature occur, because the amount of moisture carried into the furnace by the blast varies very largely with change of atmospheric conditions, and necessitates the burden of the furnace having a safe margin of fuel to allow of a sudden loss of heat from this cause.

An interesting comparison may be made between English and American blast-furnace practice. The following figures show the different conditions in typical cases (*Hiorns*):—

	Cleveland.	Pittsburg.
Cubical contents,	25,500 cub. ft.	18,200 cub. ft.
Temperature of blast.	*704° C.*	*593° C.*
Coke per ton of ore,	19·99 cwts.	16·80 cwts.
Limestone,	11·00 ,,	9·00 ,,
Ore,	48·00 ,,	32·30 ,,
Weight of blast per ton of ore,	87·15 ,,	71·20 ,,
Weight of gases,	119·50 ,,	110·10 ,,
Temperature of gases,	250° C.	170° C.
Tons of iron per 1,000 cub. ft. space produced per week,	21·57	128·0
Slag per ton of iron,	28·00 cwts.	10·70 cwts.
Calories produced per ton of iron,	88·6	69·6

In general, the English furnace has a greater capacity than

the American. Recent experience favours a more rapid working, and in the American furnace a maximum production is obtained. The great reducing energy of the American furnace with its high grade ore and fuel, its high pressure blast (10 lbs. as compared with 5 lbs. in England), and rapid working yields six times as much iron per cubic foot of space as the English furnace. An American furnace produces on an average 100,000 to 150,000 tons per annum, while some have an output of 5,000 tons pig iron per week.

In starting a blast furnace, the temperature must be slowly raised, to avoid cracking the walls of the structure. The hearth is filled with wood, and the boshes with coke. When this fuel has been ignited, the body of the furnace is filled with ore, limestone, and fuel (constituting the **burden** of the blast furnace), the materials being charged in rotation. The proportions of these materials vary according to the character of the ore and according to other conditions. The blast is gradually turned on, and after about three weeks the furnace is working at full blast. The rotation of charging is maintained until the furnace needs repair, crude iron and slag collecting at the bottom and being periodically tapped. The slag, which collects above the molten iron, is run into waggons, whilst the metal is allowed to flow into **pig-moulds** fashioned in sand to receive it. The selection and proportion of the materials to be used as flux are determined by the nature of the iron to be produced (*v.i.*), as well as upon the character of the gangue. A good blast-furnace slag must contain silica, alumina, and lime. When the gangue is chiefly argillaceous, limestone suffices as a flux; but if it be siliceous, an aluminous ore must be added; while if it be basic—*e.g.*, in spathic or oolitic ore, which contains calcium carbonate—both silica and alumina, as clay or shale, are required. A judicious mixing of ores will frequently serve the same purposes. The most siliceous slag usually made corresponds with the general formula $2RO \cdot 3SiO_2$, where RO is any base, either RO or R_2O_3. The most basic blast-furnace slags correspond with the formula $10RO \cdot 3SiO_2$. The average coke-fed furnace slag approximates to $2RO \cdot SiO_2$. Thus the selection of the fluxing material must depend upon the analysis of the ore and of the flux itself, and on the requirements of each particular blast furnace and its produce.

The following analyses are quoted by Turner as representing the composition of blast-furnace slags at Dowlais. The first is a complete analysis of an average slag. Numbers 2 and 3 are partial analyses showing the extreme variation in the composition of slags working on white iron, while the analysis of a grey

iron slag is added for comparison (No. 4). The analyses are by E. Riley :—

	1.	White Iron Slag. 2. Maximum.	3. Minimum.	4. Grey Iron Slag.
SiO_2,	41·85	45·23	39·09	38·48
Al_2O_3,	14·73	17·14	11·55	15·13
FeO,	2·63	6·91	1·29	0·76
MnO,	1·24	..	..	..
CaO,	30·99	34·32	23·81	32·82
MgO,	4·76	..	..	..
K_2O,	1·90	..	..	..
Ca,	1·15	..	..	..
S,	0·92	1·31	0·47	0·99
P_2O_5	0·15	0·43	0·10	0·15
	100·32			

Blast-furnace slag is a crude glass, sometimes opaque, and varying in colour from dark grey to light green. Slags, when acid, are permanent in air like glass, but when basic may disintegrate spontaneously by the hydration of the lime which they contain. Blast-furnace slag is practically a wasted product, but the harder kinds, if not too glassy, are profitably used to some extent for road mending, levelling waste lands, building breakwaters, and for ballast. It is also used for making bricks and cement (see Vol. II.).

The following analysis represents a slag suitable for cement making :—

SiO_2,	26·64
Al_2O_3,	18·71
FeO,	0·95
MnO,	0·08
CaO,	44·57
CaS,	1·71
MgO,	5·07
SO_3,	1·00
Water and CO_2,	0·96
	99·69

Since the introduction of the bacterial method for the treatment of sewage, slag has been used in considerable quantities for filter beds. Finally, it is converted into a product known as "slag

wool." This material is prepared by scattering a stream of slag into tenuous filaments by a jet of air or steam. It resembles glass wool in appearance, but is even more brittle, and finds application as a lagging material.

Coke is preferable to coal in the blast furnace, as it contains a smaller proportion of sulphur. Good blast-furnace coke should contain not more than 3 per cent. of moisture, 10 per cent. of ash, and less than 1 per cent. of S. It should be dense and silvery in appearance, and have an apparent density (including pores) of 0·8. Its mechanical strength should be sufficient to bear the burden of the blast furnace, and it should be capable of resisting oxidation and combustion until at the temperature of the hearth of the blast furnace.

The limestone should be non-dolomitic, and is preferably used without previous burning, as when caustic lime is charged it becomes carbonated at the throat of the furnace, and has to be reburnt lower down the body. The raw materials and products of a Cleveland blast furnace are given as follows by Turner :—

Raw Materials.	Cwts.	Products.	Cwts.
Calcined iron stone,	48	*Iron*,	20
Limestone,	12	Slag,	30
Durham coke,	20	Waste gases,	130
Air,	100		
	180		180

The changes which occur in the reduction of iron in the blast furnace are mainly influenced by the temperatures which obtain in the various parts of the furnace. These changes comprise the reduction of oxide of iron to metallic iron, the causticising of the limestone, the reduction of a portion of the carbon monoxide to carbon by the action upon it of the iron already reduced, the combination of carbon and iron to form carburetted or cast iron (which is more fusible than the pure spongy iron first produced), and the union of the lime with the gangue to form slag. Attempts have been made to map out the interior of the blast furnace into "zones," appropriate to certain reactions. According to this method of explanation the ferric oxide is reduced near the throat of the furnace at the point where the temperature has reached dull redness, the change being effected by the reducing action of carbon monoxide—which constitutes at this point about one-third of the total gases, and has been produced by the reduction of CO_2 generated by the fuel in the lower part of the furnace. The reaction is accompanied by an evolution of heat.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 8{,}652 \text{ Cal.}$$

Spongy iron disseminated through gangue results, and as it descends into the body of the furnace it is partly oxidised by more CO (which is capable, according to the temperature, of *acting as an oxidising and as a reducing substance*) with the liberation of carbon. Doubtless the ferrous oxide is again *mainly reduced before fluxing as but little iron appears in the* slag. The reduction is completed, probably (at the belly), by the solid carbon present, some of which is supplied by the dissociation of carbon monoxide, which takes place at high temperatures with formation of carbon dioxide and free carbon. The reactions of carbon monoxide in the blast furnace are somewhat complicated, being influenced largely by physical conditions, such as mass, temperature, and pressure, and also by the texture of the materials used. The finely-divided carbon and *iron unite to form fusible carburetted iron which is melted* in the boshes at the same time as the fluxing of the gangue takes place. The causticising of the limestone occurs at a point rather below that at which reduction of iron oxide begins.

The powerful reducing atmosphere of the blast furnace and the high temperature obtaining therein, cause the reduction of other substances than iron, chiefly manganese, silicon, and phosphorus, while sulphur (mainly from the fuel) is retained unoxidised, and appears together with the above-mentioned bodies in the crude iron. On account of the simultaneous presence of a high temperature, basic material (alkalies from the ore, etc.), carbon and nitrogen, alkali cyanides are produced in the normal working of the blast furnace. The quantity of cyanogen thus escaping may amount to 6 grms. per cubic metre of the waste gases. When titanium is present in the ore (*e.g.*, as TiO_2 in clay) nitrogen is fixed as nitride as well as cyanide, large crystals of the compound $TiCy_2 . 3Ti_3N_2$ being produced. These constitute infusible masses, called "bears," in the blast furnace, and much impede the working.

A compact incrustation of "furnace-calamine," consisting chiefly of oxide of zinc, is found round the throat of the furnace in smelting zinciferous iron ores, no less than 100 tons of this compound, termed "Gichtschwamm," being obtained annually from the furnaces at Aix-la-Chapelle.

The limit to the efficiency of a blast furnace regarded as a heat-machine appears to be determiued by the fact that carbon monoxide ceases to be efficient as a reducing agent for ferric oxide, at the temperature obtaining at the throat of the furnace, when it is so diluted with CO_2 that the ratio of the carbon which they respectively contain falls below 2 : 1. Thus the difference between the heat produced by the combustion of carbon to CO_2

and of carbon to CO (viz., 5,600 Cal. per kilo.) is lost so far as the furnace is concerned, but is largely recovered by the use of the hot blast stove.

About 40 per cent. of the total quantity of heat in the blast furnace is consumed in reducing the iron to the metallic state, 10 to 12 per cent. in the fusion of the iron, and 12 to 15 per cent. in the fusion of the slag, the balance being accounted for by the reduction of impurities, the causticising of the limestone, the reduction of CO_2 from the limestone to CO, and the carburising of the iron, while another large item (about 10 per cent.) is the heat going away with the waste gases; this, however, is mostly recovered.

About 75 per cent. of the total calorific value of the fuel is realised in the blast furnace, on which account it may be reckoned an efficient machine.

The crude iron produced is run from the furnace into sand-moulds, producing **pig iron**; here a portion of the carbon taken up by the iron in the furnace separates from solution in the metal in the form of graphite. A portion of this graphite floats to the surface of the metal as "kish," the remainder being still associated with the metal itself.

When the bulk of the carbon thus separates, the metal is known as **grey** iron; when partial separation takes place **mottled** iron is produced; while when the separation is at a minimum the material is called **white** iron. The production of grey iron occurs in those furnaces which work with siliceous ores and a high percentage of fuel at a high temperature; silicon is then present in the pig, and induces the crystallisation of the carbon as graphite. White iron, on the other hand, is made in heavily burdened furnaces, working with the minimum of fuel (and at lower temperatures), and contains but little silicon, on which account the separation of graphite does not take place.

The composition of grey and white cast iron is given below:—

	Grey.	White.
	Per cent.	Per cent.
Graphitic carbon,	3·30	...
Combined carbon,	0·20	3·20
Silicon,	3·50	0·64
Phosphorus,	0·98	1·32
Sulphur,	0·02	0·20
Manganese,	1·58	0·60
Iron (by difference),	90·42	94·04
	100·00	100·00

The way in which the metal is cooled also influences the form in which the carbon occurs, slow cooling promoting the crystallisation of graphite and consequent production of grey iron, whilst sudden cooling favours the production of the more homogeneous white iron. Chilled castings are an illustration of this.

White iron is principally used for the production of malleable iron. For this object it is advantageous that it should contain as little carbon as possible and have a low content of silicon, phosphorus, and sulphur. Its specific gravity is 7·5, as against 7·1 for grey iron. It is harder and more brittle than grey iron and somewhat more fusible. Grey iron is used for foundry purposes and steel making. The classes of grey iron richer in graphitic carbon are better mixed with poorer varieties when used for castings. It is this need for mixing which makes casting directly from the blast furnace undesirable, apart from question of convenience. For foundry work the metal is melted in a cupola furnace—a small intermittently worked blast furnace—into which pigs and coke are fed. By thus melting iron in air the proportion of silicon and manganese is steadily diminished, and the carbon is gradually changed from the graphitic to the combined form. At the same time, sulphur may be absorbed from the furnace gases, while the percentage of phosphorus and total carbon may be somewhat increased, due to concentration in a smaller quantity of metal. The physical effects produced on the iron are in accordance with these chemical changes.

Pig iron is graded, according to its colour and texture, in numbers from 1 to 8, or more commonly Nos. 1 to 4 for foundry purposes, together with "No. 4 forge," "mottled," and "white." No. 1 is the greyest and richest in silicon, and in passing from No. 1 to white iron the combined carbon gradually increases and the silicon diminishes (see also p. 15).

By varying the working of the blast furnace, the crude iron may be made to contain varying proportions of sundry metallic, as well as non-metallic, impurities, whereby its character is much modified. Thus, pig iron rich in silicon (**ferro-silicon**), constitutes a light coloured "glazy" iron useful in the cupola for producing grey iron from white pig. By reducing manganiferous ores in a blast furnace, various grades of manganiferous pigs are made. The presence of manganese causes the crude iron to contain more carbon than does normal pig (4 to 6 per cent. all in the combined form), the alloy having a crystalline structure and lustrous appearance, justifying its name **spiegel-eisen** (*mirror-iron*).

Spiegel-eisen contains about 10 per cent. of manganese, and when this proportion is largely increased (with a practicable

maximum of 85 per cent.) the metal is called **ferro-manganese.** Both grades are used in steel making (*v.i.*). For some purposes iron rich in both *silicon* and *manganese* is produced, and is known as "silico-spiegel." Typical analyses of these iron alloys are given :—

	Ferro silicon.	Spiegel-eisen.	Ferro-manganese.	Silico-spiegel.
	Per cent.	Per cent.	Per cent.	Per cent.
Si.	14·000	·110	·970	10·740
Mn.	1·950	8·110	80·040	19·640
S, ...	·078	. .	. .	. .
P, ...	·076	·080	·175	0·074
C, graphitic. . .	1·200	. .	. .	0·330
C, combined. . .	·230	4·270	6·530	1·850
Fe.	82·466	87·40	12·230	67·560
	100·000	99·970	99·945	100·194

Ferro-chromium, made by reducing chrome iron ore, contains 40 to 70 per cent. of chromium, and is also used in steel making, particularly for armour-piercing projectiles, and special steels for tools and motor car parts. When prepared in the ordinary way, ferro-chromes, like ferro-manganese, always contains a high proportion of carbon, the percentage of which increases with that of the chromium. For certain purposes low carbon ferro-chrome is required, and is produced from pure oxides of chromium by the thermite process, or in the electric furnace.

Other ferro-alloys, such as ferro-vanadium and ferro-tungsten, are made in a similar manner. Ferro-titanium has recently received the attention of metallurgists, and will doubtless have a more extended application when its properties become better known, and the methods of production improved and cheapened. Titanium itself may be prepared by the Goldsmith thermite process, while Rossi produces ferro-titanium by means of a mixture of titanic ore, aluminium, and scrap iron in suitable proportions in an electric furnace.

Ferro-aluminiums, containing 5, 10, 20, or other percentage of aluminium, are prepared by melting the materials in crucibles, or by the use of the electric furnace; they are employed for steel making to give soundness to the ingot, and in the foundry to produce soft, grey castings. Phosphoric pig iron, containing as much as 7 per cent. of phosphorus, is manufactured for the basic steel process from ores rich in phosphorus, or by the addition of basic slag to the charge.

The fact that graphitic iron (grey iron) is readily convertible into carburetted iron (white iron) by rapid cooling (which prevents the separation of graphite), allows of the production of chilled castings by pouring molten grey iron into moulds, which are constructed of massive iron, at such points of the casting as are to be chilled. The surface immediately in contact with the cold iron is converted into hard white iron to the depth of $\frac{1}{8}$ inch or more. This method is used for rolls and railway carriage wheels, the latter being employed in American engineering practice (*cf.* p. 16).

Pig iron from the blast furnace is of low tensile strength (about 7 tons per square inch) and comparatively brittle. At the same time it is not malleable and cannot be welded. Thus, while cast iron has the special application indicated by its name, its value for structural uses, where tensile strength and ductility are required, is small.

In early days and among primitive peoples, pure iron was reduced directly from the ore, the production of fusible impure iron, such as is obtained from the blast furnace, constituting a later stage of development. The direct production of iron is only practicable, as has been already mentioned, from pure ore (*e.g.*, rich magnetite) and pure fuel—viz., charcoal. The modern large demand for structural iron of high tensile strength renders it impossible to obtain a sufficient supply from these comparatively scarce materials. Hence it is necessary to produce a crude metal, and to refine this to the desired degree of purity.

The methods for the direct production of wrought iron from the ore are comparatively unimportant. The process is still employed by savage races who make iron, and also in places where the character of the ore, the fuel, or other conditions render the adoption of the blast furnace impracticable. Judged by its annual output, the most important process is that of the *American Bloomery*, employed in the Eastern States, where charcoal and rich magnetic ores are available. The reduction is performed in a water-cooled iron hearth with a hot blast. In India the natives use both open hearths and small blast furnaces. In certain European localities—*e.g.*, Spain—a peculiar hearth, known as the "Catalan forge," is still employed. Of course, a large number of processes have been suggested or introduced for the production of commercially pure iron direct from the ore, but not one has proved itself capable of competing with the indirect blast-furnace process. For details of these processes the larger metallurgical works should be consulted (*e.g.*, Percy's *Iron and Steel*, and Turner's *Iron*). The disadvantages inherent in such processes are that the yield in a given time is relatively

small, while the cost of labour and fuel and the loss of iron in the slag are relatively great.

For the better realisation of the relation between crude iron and the products of its purification, the following method of classification, which is based on that which is official in Germany, may be quoted (*Ost*) :—

Crude Iron	*Malleable Iron*
Contains over 2·3 per cent. of impurities; *generally 9 to 10 per cent* (C, 2 to 5 per cent., together with Si and P) melts without passing through any well-marked pasty stage, is therefore not malleable; brittle at the ordinary temperature.	Contains a smaller proportion than 2·3 per cent. of *impurities, chiefly* carbon, generally under 1 per cent.; higher fusing point than crude iron, increasing as the impurities decrease; softens gradually on heating up to its fusing point, and is therefore malleable. Those kinds which are markedly poor in impurities are malleable when cold.
A. **Grey Iron.**—The bulk of the carbon is graphitic, giving a grey fracture.	A. **Puddled Iron.**—Prepared in a pasty, imperfectly fused state, therefore not homogeneous; contains intermixed slag. *Varieties containing* more carbon are termed **puddled steel.**
B. **White Iron.**—The bulk of the carbon is combined, and is not present as graphitic carbon.	B. **Ingot Iron** (mild steel).—Prepared perfectly fluid, therefore homogeneous and free from slag. The harder varieties, containing more carbon, may be called ingot steel.*
C. **Spiegel-eisen and Ferro-manganese.**	C. Special varieties, including **malleable cast iron** and **temper steel**—*e.g.*, **cementation steel.**

The essential difference between **cast iron, steel,** and **wrought iron** (using these terms in their common acceptation) lies in their varying content of carbon. Ideal cast iron consists of Fe with 3 to 5 per cent. of C as *graphite*; ideal steel of Fe with 0·5 to 2·0 per cent. of combined C; ideal wrought iron of Fe with under 0·1 per cent. of C. Intermediate percentages of C give products approximating to one or other of the materials thus classified. From this it follows that ideal cast iron and ideal wrought iron, when mixed in suitable proportions, would yield steel if the appropriate change in the condition of the carbon were effected. With commercial metals the production of steel by the mixture of cast and wrought iron is generally impracticable on account of the presence of impurities—*e.g.*, phosphorus—which, although of small account in cast or wrought iron, are highly deleterious to steel. The production of steel, therefore, involves more roundabout methods than would appear

* Used for large steel castings.

from its mere percentage of carbon. These will be described in due course.

PURIFICATION OF CRUDE IRON.—Most of the impurities of crude iron, notably carbon and silicon, are more easily oxidisable at high temperatures than is the metal itself, whence it follows that all processes of purification, except that by electrolysis, depend on the removal of the impurities by limited and regulated oxidation, which may be effected either partly by solid oxidants—*e.g.*, in puddling—or by air, as in the Bessemer process. The carbon is removed as gaseous oxides, the silicon as SiO_2, and the phosphorus as P_2O_5, the last two acid oxides being more readily eliminated in the presence of a strong base—*e.g.*, FeO or CaO.

1. **Purification without Complete Fusion of the Product.**—As has been stated above, white iron is better adapted than grey for conversion into malleable iron by puddling, because its comparatively low content of silicon causes it to pass through a pasty stage before fusion, the advantage of which will be gathered from the description of the puddling process (*v.i.*). Grey iron melts more sharply than white, and, therefore, can be oxidised by a gaseous oxidant injected through it more readily than by treatment with a solid oxidant. Oxidation with air blown through the metal is comparatively modern, wherefore the production of malleable iron from grey iron was formerly necessarily preceded by the conversion of the grey iron into white iron. This process was conducted in the refinery—the term being a misnomer as the product is not sensibly refined, but merely converted into white iron. The German phrase *weissmachen* (whitening) is more appropriate.

The **refinery hearth** consists of a rectangular cast-iron bed, the floor of which is of sandstone, and the sides hollow and water-cooled. A chimney surmounts the hearth, and upon the latter air is directed through twyers at a pressure of 2 to 3 lbs. per square inch. The floor is protected by a layer of broken sandstone which soon fluxes to a glaze. The charge of grey pig, or of molten iron direct from the blast furnace, mixed with coke, is kept under blast for about two hours, during which time the iron forms a layer beneath the fuel, but is oxidised by the air directed downwards upon it. The silicon is the main impurity oxidised, carbon and phosphorus being but little affected. Thus, the slag is a nearly pure ferrous silicate approximating in formula to $2FeO . SiO_2$. The white iron is run into chilled moulds in the form of plates 2 to 3 inches thick, which are brittle enough to be afterwards easily broken. The refining proper (as distinct from "whitening") of the metal thus obtained was originally effected

in an open hearth, which consisted of a forge worked with a blast. *In this forge, fuel (charcoal) was first raised to incandescence*, and the iron piled on top. After a time the metal melted and trickled through to the bottom of the hearth, passing through the stream of air from the twyer on its way. Basic silicates of iron were thus formed, and a certain amount of decarburation occurred, so that the mass became pasty; it was then balled and replaced on the top of the fuel, its passage to the bottom and oxidation being repeated. Finally, the "bloom," or mass of pasty metal, was beaten under a tilt hammer to express slag. In this operation oxidation is effected both by solid oxidants (oxides of iron) and by air.

This process, known as the South Wales process, has been almost completely abandoned in this country in favour of the manufacture of steel, and is only used to a limited extent for the production of "best charcoal iron."

The **puddling process,** introduced about 120 years ago, differs *from the open-hearth process, in that the metal is heated by the* combustion of gases instead of by direct contact with solid fuel. The solid fuel whence the gases are produced may, therefore, contain sulphur, the SO_2 given off on combustion not being absorbed by the iron. The need for a non-sulphurous fuel such as charcoal is thereby obviated. The reverberatory furnace shown in Fig. 15 is the oldest form of furnace for this purpose, and provides gaseous fuel in precisely the same manner as the modern gas producer does (see p. 80). The bed of the reverberatory furnace which forms the puddling furnace is of cast-iron plates, supported on wrought-iron bars, which allow of free circulation of air, whereby the plates are cooled. This bed is protected by a lining or "fettling" of hammer slag squeezed from the bloom (*v.i.*), and a superficial layer of nearly pure oxide of iron—*e.g.*, hæmatite—the whole being so moulded that a saucer-shaped depression is formed. In older forms of the process, known as **dry puddling,** "refined"—*i.e.*, white iron (*v.s.*)—was used and heated until it became pasty and partly oxidised, when it was broken up and continuously stirred to mix it with the oxide formed. In the modern method of puddling—"pig-boiling"—grey iron is used, and allowed to become perfectly fluid before stirring with oxide of iron, which is provided in this case by the fettling. During this incorporation the temperature of the furnace is lowered, and slags containing oxide of iron are added to flux the silica formed by the oxidation of the silicon of the pig. *It is sometimes the custom to make certain additions* of "physic" (usually quack preparations) during the early stages of the puddling process to assist oxidation. The most usual is

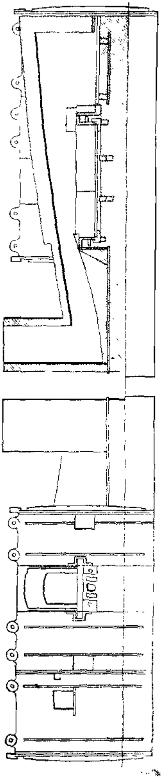


Fig. 15.—Reverberatory furnace (vertical elevation and section).

a mixture of manganese dioxide and salt; the former supplies additional oxygen and promotes fluidity, while the salt, being decomposed by silica, possibly assists in the more complete removal of phosphorus as chloride. Usually, however, the proportions of "physic" added are too small to produce any marked effect. When the blue flame of CO, due to the oxidation of the carbon of the pig by the oxide in the slag, is perceived, the temperature is raised, to compensate for the decreasing fusibility of the iron as its impurities are removed. The charge is now "rabbled"—*i.e.*, swept from the centre towards the circumference of the hearth by an iron bar—during which process the ebullition of the mass caused by the escape of CO decreases, and the iron "comes to nature." After another thorough mixture the metal is agglomerated into balls, which are brought to a welding heat and withdrawn from the furnace. It is then strongly compressed either by blows from a steam hammer or by means of a squeezer consisting of a lever, on the principle of a pair of nut-crackers, working against a bed plate. The slag is thus squeezed out, and a "bloom" of wrought iron is obtained which can be rolled down into bars by passage between grooved rollers. The iron is rendered more nearly homogeneous and its quality improved, by cutting the puddled bar into lengths, **piling** it, re-heating in a reverberatory furnace, and again hammering and rolling. These reverberatory furnaces are similar to those used for puddling except that the beds are flat and slope

downwards towards the flue, at the bottom of which the "flue cinder" flows out. For re-heating furnaces gas-producers (with the usual regenerators) are often employed. A modern Siemens furnace, as used for puddling and reheating, is shown in the accompanying illustration. The iron thus improved is of the grade known as "merchant iron."

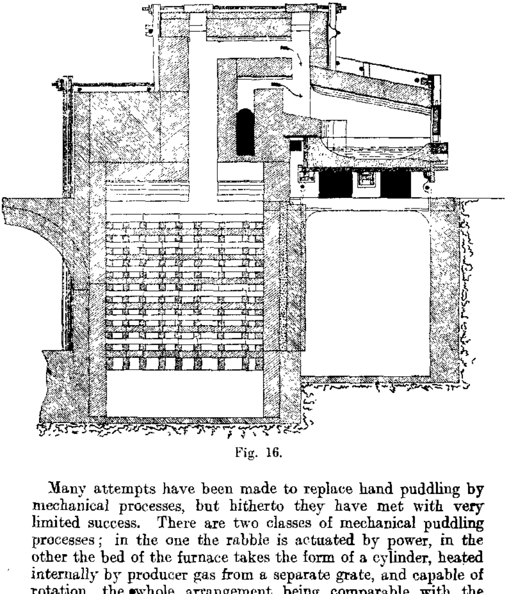


Fig. 16.

Many attempts have been made to replace hand puddling by mechanical processes, but hitherto they have met with very limited success. There are two classes of mechanical puddling processes; in the one the rabble is actuated by power, in the other the bed of the furnace takes the form of a cylinder, heated internally by producer gas from a separate grate, and capable of rotation, the whole arrangement being comparable with the revolving black ash furnace (see *Alkali*, Vol. II.). The cylinder is lined with oxide of iron fettling, which is brought into contact with the charge and effects decarburation. The following

analyses (*Turner*) show the composition of puddled bar and of the finished wrought iron The impurities are largely derived from interstitial slag, which may be present to the extent of 1 per cent., or even more:—

	Puddled Bar.	Wrought Iron.
	Per cent.	Per cent.
Carbon.	0·10	0·06
Silicon.	0·13	0·04
Manganese.	0·08	0·08
Phosphorus.	0·35	0·20
Sulphur, ...	0·05	0·05
Iron (by difference).	99·29	99·57
	100·00	100·00

The output of wrought iron by puddling crude iron is about 90 to 94 per cent. of the iron charged.

Chemistry of Puddling.—The process of puddling is conducted essentially for the selective oxidation of the impurities of the crude iron, but at the same time the charge must be mechanically worked, not only to expose ample surface to the incoming air, but to cause the slag (formed by the impurities), which is intimately emulsified with the metal, to run together and agglomerate in distinct drops easy of expression under the hammer. In common with other processes for purifying iron, puddling first causes the elimination of silicon and manganese, carbon, sulphur, and phosphorus being removed at a later stage.

Of the two principal theories of puddling which have been suggested—viz., Siemens' magnetic oxide theory, and the ferric oxide theory of Snelus—the former is most usually accepted. According to this theory the oxidation of the silica and carbon is entirely due to the fluid oxide of iron present in the "cinder," which may be taken to consist of magnetic oxide Fe_3O_4 and ferrous silicate. Indeed, it seems doubtful whether ferric oxide Fe_2O_3 ever exists as such in fluid cinder.

In the ordinary process of puddling there are two varieties of cinder produced, differing somewhat in composition. The first variety is known as "boilings," from the fact that it boils over the foreplate during the heat. The second kind is "tapped" out at the end of the process, and is known as tappings. The following typical analyses show that the "boilings" are richer in phosphorus and silica than the "tappings" (*Turner*).

	Boilings.	Tappings
	Per cent.	Per cent.
Fe_2O_3,	6·94	12·90
FeO,	62·61	64·62
SiO_2,	19·45	15·47
P_2O_5,	6·32	3·91
Minor constituents,	4·68	3·10
	100·00	100·00

If the removal of carbon from crude iron by puddling be stopped before the stage corresponding with wrought iron is reached, a steely iron, called **puddled steel,** is obtained. A pure raw material must be employed, as the influence of sulphur and phosphorus upon steel is more deleterious than upon wrought iron. Modern steel-making processes have displaced this method.

Puddled iron is a definite variety of malleable as distinct from crude iron, by reason of its structure. Having never been fused, and having been repeatedly hammered and rolled, it consists of a mass of parallel fibres arranged to form laminæ, each of which may be regarded as the representative of a member of the "pile." Between adjacent fibres and laminæ, slag, which has escaped expression, exists and renders the metal non-homogeneous. Malleable iron which has been produced by methods involving perfect fusion, and is, therefore, homogeneous and substantially free from slag, is now largely made by processes originally devised for the production of steel. Such "ingot iron," commercially known as "mild steel," is produced by the decarburation of cast iron by the open hearth and Bessemer processes now about to be described (the properties of wrought iron are considered on p. 17, *et seq.*)

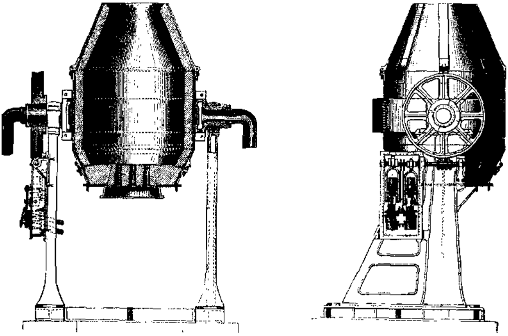
2. **Purification of Iron by Methods Involving Complete Fusion of the Product.**—These methods, which have been adopted within the last thirty years, are typified by the **Bessemer process** and the **Siemens Martin process.**

The Bessemer process consists in blowing air through fused pig iron whereby the impurities present are successively oxidised and an approximately pure iron results, to which carbon is restored (in quantity depending upon whether an ingot iron or a steel is required), by the addition of a material rich in carbon —*e.g.*, spiegel-eisen.

The process is almost unique among our large manufacturing industries in that it is carried on to-day substantially in the same manner as when it was originated some 50 years ago; the

only improvements that have been introduced being in detailed mechanical arrangements and larger appliances.

The operation is conducted in a "converter," shown in Fig. 17. This consists of a shell of steel plates with a refractory lining and carried by trunnions on which it can be rotated for filling and emptying. The converter is made in two forms, known as the concentric and eccentric, according to the shape of the nose or upper section. The latter form has the upper part of the converter straight on one side and curved on the other, while in the concentric one (illustrated in the figure) this part forms the frustrum of a cone, the sides being equally inclined to the axis of the converter. An air blast is supplied through pipes (which



A. B.

Fig. 17.—Walker's 10-ton converter.
A, Vertical section. B, Side elevation.

pass through the trunnions), whence it travels to the air box at the bottom of the converter, and thence by twyers to the interior. The bottom of the converter being the portion subjected to the greatest wear, and requiring to be frequently renewed, is made so as to be easily replaced. The usual size takes a charge of about 10 tons. As originally devised, the Bessemer converter was lined with **ganister,** a highly siliceous material, refractory at high temperatures. The acid character of this lining did not

allow of the employment of iron from phosphoric ores, as the *elimination of phosphorus only takes place freely in the presence* of a base capable of forming a stable phosphate with the oxidised phosphorus. Pure hæmatite pig has, therefore, to be used in an acid-lined converter. *The chief essentials in its composition* are a very low percentage of sulphur and phosphorus, with about 2 per cent. silicon. Grey iron is more suitable for the acid process than white iron, on account of its greater fluidity and its low sulphur content; moreover, its carbon being in the graphitic form, the production of carbonic oxide at too early a stage in the process is not so probable as with white iron. The silicon is a more important source of heat than is the carbon, on account of its high heat of combination with oxygen. In order to blow iron containing less than 1 per cent. of silicon, successfully, the heats must follow each other quickly, and the vessels and ladles must be very hot. Quick blowing and short intervals is characteristic of American practice. The greater the percentage of silicon the hotter is the charge, the longer the blow, the greater the loss, and the more expensive the repairs and maintenance. If, however, the silicon is too low, it causes cold heats and bad working generally. Howe considers that 1·25 per cent. is the best proportion. In England, where high silicon irons are commonly available, the aim is to keep the silicon sufficiently low, whilst in Sweden it is just the reverse. A pig such as is used in this country, and the iron produced from it, have the following compositions :—

	1. Bessemer pig.	2. Metal at end of blow.	3. After addition of spiegel.
	Per cent.	Per cent.	Per cent.
Carbon,	3·57	0·19	0·37
Silicon,	2·26	Trace	Trace
Manganese,	0·04	Trace	0·54
Sulphur,	0·10	0·10	0·09
Phosphorus,	0·07	0·07	0·05

The molten metal for supplying the converter may be melted in a cupola, or taken direct from the blast furnace, or from the latter to a receiver or mixer before finally passing to the converter. The modern cupola is really a small blast furnace. In some cases the outside shell will be 10 to 12 feet in diameter, and the blast pressure as much as 2 to 3 lbs. per square inch. It is usually lined with firebrick and ganister.

According to the best practice, uniformity of raw material is secured by mixing the product of several blast furnaces—thus avoiding the effect of individual irregularities of working—and running the still liquid metal into a tipping ladle, whence it is transferred to the converter. An extension of this principle has been adopted by J. Massenez, who combines the process of mixing with a method of **desulphurisation,** the two operations being carried out by the plant shown diagrammatically in Fig. 18. The cast iron is tapped from the furnace into a ladle which is run by a locomotive to the mixer shown in the middle of the figure, and is then treated with sufficient ferro-manganese to remove the bulk of the sulphur as MnS, which floats to the top. The desulphurised iron is turned into a second ladle, shown

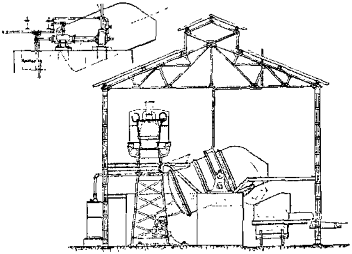


Fig. 18.—Mixer and desulphuriser.

on the right-hand side of the figure, and is conveyed to the converter (*q.v.*).

The converter is previously heated by a charge of burning coke which is raked out before the vessel is filled. The blast (usually 20 to 25 lbs. per square inch) is started, and the converter, which was turned over to receive the charge, is raised to a vertical position. The silicon and manganese in the iron are first oxidised and the temperature considerably raised by their heat of combustion. A slag of manganous and ferrous silicates is thus formed. In consequence of the products of combustion being solid, but little flame is visible at the mouth of the converter at this stage of the process, which lasts for some six minutes. As the silicon is removed, the graphitic carbon becomes converted into combined carbon and then burns, the charge boiling

from the escape of CO, which burns at the mouth of the converter, accompanied by a shower of particles of burning iron. If the blow is too hot, as indicated by the appearance of the flame, scrap steel is added to lower the temperature. This second stage occupies another six minutes. During a third period of six minutes the flame dies down, and is succeeded by a stream of white-hot nitrogen from the air of the blast, the oxygen of which is retained by the charge. A certain amount of both iron and manganese is volatilised during the second and third stages of the blow, when the metallic vapours are carried out and burnt with the carbon monoxide. From the composition of this "fume"—FeO 16·29, MnO 48·23, SiO_2 34·86 per cent.—Prof. Hartley suggests the volatilisation of free or combined silicon. Probably the "fume" is partly caused by the mechanical action of the blast. The metal now contains mere traces of impurities (see table above), but is slightly oxidised. The converter is inclined, and a charge of spiegel-eisen added, the amount being dependent on the grade of the required product. The addition of manganese in some form is absolutely essential in ordinary cases, as without it the steel is quite unworkable. The contents of the converter are finally emptied into the ladle, whence, after its temperature has fallen sufficiently so that it pours quietly and is capable of yielding a sound casting, the metal is allowed to flow into vertical cast-iron ingot moulds. The effect of the spiegel-eisen is shown in column 3 in the above table. When a metal very low in carbon—*e.g.*, 0·25 per cent. is required, ferro-manganese is substituted for the spiegel-eisen, as by this means for a given content of manganese a smaller proportion of carbon is introduced. It is not found advisable to dispense with the use of spiegel-eisen or of ferro-manganese by stopping the blow when the metal contains a residual amount of carbon identical with that required in the finished product, as it is less easy to hit the precise point than to almost completely decarburise the metal, and then restore * carbon to it in known amount. Moreover, it is probable that manganese has a beneficial effect as a de-oxidant.

Occasionally, however, in Sweden, when the amount of manganese in the pig is above 2 per cent., the direct method is adopted —that is, the blow is not continued till the whole of the carbon is burnt off, but stopped when the metal contains the desired amount of carbon, which is judged by the aid of the spectroscope and the colour of the slag.

In regard to the mechanism of the reactions taking place in

* Carbon as such has been proposed as a substitute for ferro-manganese or *speigel-eisen* (*cf.* Darby process, p. 209).

the converter, it cannot be supposed that traces of impurities are seized by the oxygen out of the large mass of metal and oxidised directly, but it is generally admitted that the oxidation is an indirect reaction, magnetic oxide being first formed near the twyers, and, acting as a carrier of oxygen to the impurities in the bath, is reduced by these impurities to FeO and Fe as it passes upwards.

The need for utilising phosphoric pig has led to the use of a basic instead of an acid lining. Thus, in the Thomas-Gilchrist process, the converters are lined with dolomite, which is either made into bricks or mixed with tar and rammed *in situ*. Since grey iron generally contains much silicon, it is unsuitable for the basic process. White iron contains only a moderate amount of silicon, and is often high in phosphorus, which, being a good heat producer, and playing a part similar to that of silicon in the acid process, is required in the basic process. In fact, a certain percentage of phosphorus is as essential to the basic process as a certain percentage of silicon is to the acid process. In practice 2·5 to 3·0 per cent. of phosphorus is found to give the best results. Pig iron containing much less phosphorus than this does not give satisfaction. The charging and blowing are conducted as in the acid process, save that *before charging about 10 to 15 per cent. of quicklime, calculated* on the weight of the charge, is introduced, and the blow is continued past the point at which the consumption of the carbon is complete, this second period being known as the "after-blow"; during this time the phosphorus, which is the last impurity to be burnt, is oxidised and combines with the lime to form the basic slag, which is used as a fertiliser (see *Manures*, Vol. II.), or for producing phosphoric pig in the blast furnace. The production of pig rich in phosphorus is necessary, as iron poor in phosphorus, though still containing too much to be dealt with by the acid process, cannot be treated in the converter as satisfactorily as can that rich in this element. Silicon is more completely removed than in the acid process, the reverse being the case with manganese. Sulphur is removed almost entirely during the "after blow" in the form of calcium sulphide by the action of the fluid calcareous slag, possibly with the assistance of manganese, which may also play some part in its elimination. The basic slag is poured off and spiegel-eisen introduced, followed by ferro-manganese, which is added to the metal in the ladle. The following analyses illustrate the changes which occur in the composition of the metal:—

	1. Basic pig.	2. Metal at end of after-blow.	3. Finished metal.
	Per cent.	Per cent	Per cent.
Carbon,	3·57	Trace	0·12
Silicon,	1·70	..	0·03
Phosphorus,	1·57	0·08	0·02
Manganese,	0·71	Trace	0·27
Sulphur,	0·06	0·05	0·04

The chief improvements in the basic Bessemer process in recent years have been the introduction of processes such as those of Flohr, and Massenez, involving the addition of oxides of iron in the converter, with the object of increasing the fluidity of the slag and decreasing the waste. The greatest drawback to the use of Cleveland pig iron in the basic converter is its high silicon content. When blown directly this causes rapid wearing of the linings, and also forms an acid slag which reacts violently with the basic slag, resulting in quantities of slag and iron being blown out and consequent fluctuating yields. Moreover, a large slag volume is inevitable because of the excessive amount of lime necessary to neutralise the SiO_2 and P_2O_5, and as a result the slag is low in P_2O_5, and commands a low price as a fertiliser. It was even found necessary in the Cleveland district to import foreign ores to mix with the Cleveland stone to make an iron low in sulphur and silicon with high phosphorus. The **Massenez process** is especially adapted for the manufacture of steel from high-silicon phosphoric pig iron by the basic Bessemer process. Some iron oxide is first put into the converter with or without a small quantity of lime and the molten Cleveland pig iron (Si 1·5 to 3·0 per cent., P 1·45 to 1·55 per cent.) poured in. The metal is blown till all the Si is oxidised, and the converter then turned down and as much of the slag as possible poured off. The slag contains Fe 3 per cent., SiO_2 35 to 45 per cent., and no phosphorus. Owing to the low temperature during the first blowing it affects the basic linings but slightly. The slag after the second blowing contains Fe 8 to 11 per cent., SiO_2 11 to 12 per cent., P_2O_5 14 to 20 per cent. The oxide added is completely reduced. The working of the process is clean, and the steel produced is regular in quality.

The high temperature produced by the oxidation of silicon in the Bessemer process is favourable to the burning out of the carbon, which occurs next, but unfavourable to the combustion of the phosphorus. The **Flohr process** introduced at Dudelingen

consists in adding, at the end of the decarburising period, specially prepared briquettes of mill cinder and lime. A reduction in temperature arises partly from the withdrawal of the heat necessary to heat the briquettes and to dissociate the $Ca(OH)_2$ and water resulting from it, and partly from the reaction between the iron phosphide in the bath and the ferrous oxide from the briquettes—

$$5FeO + 2Fe_3P = P_2O_5 + 11Fe.$$

The dephosphorisation is, no doubt, aided by the finely divided lime resulting from the disintegration of the briquettes ready to form calcium phosphate. The advantages claimed for the process are a reduction in loss of metal either by oxidation or projection, a saving in lime required, an increase in the phosphorus content of the slag, and a greater permanency of the converter bottoms and linings.

Although the general tendency has been to increase the capacity of the converters and the general adoption of bottom blowing, the small converter with side blowing is still used, mainly to produce very soft, low carbon steel, or more especially steel for the manufacture of castings. These processes, such as the Clapp Griffiths, Robert, Tropenas, etc., vary more in their mechanical details than in any essential differences in the processes themselves.

The Siemens-Martin or Open-Hearth Process.—The production of refined iron from crude iron can be effected in "open" hearths heated by regenerative gas furnaces (see Fig. 8, p. 84), as well as in converters. There are two forms of this process, the Siemens-Martin, in which a mixture of pig iron and scrap wrought iron is used, and the Siemens, in which pig iron and iron oxide (pure ore) are employed. In the first case the reduction of the content of pig iron in carbon and other impurities is effected (*a*) by dilution with the less impure scrap,* and (*b*) by the selective oxidation of the fused metal by the furnace gases. In the second, the oxidation of the carbon, etc., of the pig is performed by the oxygen of the ore as well as by the furnace gases. The saucer-shaped hearth of the furnace A, which in modern practice often has a capacity of 40 to 50 tons, is made of iron plates (kept cool by circulation of air beneath them) and is packed with highly siliceous sand, or, in the case of the **basic open-hearth process,** with dolomite or magnesite burnt and ground with tar. When the furnace is white-hot, red-hot pig iron is charged, and when this is fused, scrap iron or ore (or

* Which is useless until it has been remelted and recovered as massive metal.

both) is gradually added. The proportion of pig to scrap varies according to the composition of both and of that of the metal to be produced. A usual proportion is about 1 of pig to 3 of scrap. After each addition of scrap the charge is well stirred, and when complete admixture has taken place, samples are withdrawn and tested, and pig or scrap added according to requirements. Owing to the complete control of which gas firing allows over the heating of the furnace, the exact adjustment of the compositiou of the bath of fused metal can be attained by repeated tests and additions of the component materials. When using a basic lining, a phosphoric pig may be worked, and lime is added to the bath. As in the basic Bessemer process, the complete removal of carbon is needed to ensure oxidation of the phosphorus. Whichever process is worked, the final adjustment of the content of carbon is effected by the addition of ferro-manganese as in the Bessemer process. To insure solid castings in basic open hearth work a higher proportion of silicon is required than can be obtained in the pig iron fulfilling the requirement of the furnace. The additional silicon is added in the form of ferrosilicon or silico-spiegel (*q.v.*), while more recently silicon carbide has also been used. Other elements used to procure solidity are manganese and aluminium; the latter has, to a considerable extent, replaced ferrosilicon for this purpose. These elements (Si, Mn, and Al) seem to act partly by deoxidising the iron and carbon and partly by increasing the solvent power of the solid metal for gases, so that a less amount separates out on cooling. Recently titanium in the form of ferrotitanium has been used to secure homogeneity in the steel; it probably does this by combining with both oxygen and nitrogen present in the metal. The process takes about eight to ten hours, and the loss of metal amounts to 5 to 7 per cent.

In order to hasten the operation, the pig iron may be charged into the furnace in a molten state. So far as the acid open-hearth process is concerned, there is probably little advantage in using molten metal, as it is not possible to add oxides of iron on the silica hearth of the furnace to effect rapid oxidation of the impurities, and it has not been generally adopted. When cold materials are charged, the large size of modern furnaces necessitates mechanical charging, and this has been met by the "Wellman charger" and similar machines, by which the materials are charged about 1 ton at a time from boxes. In basic open hearth works the best practice is to take molten metal, previously subjected to a preliminary refining in a "mixer," direct to the open-hearth furnace, some of the ore and lime having been previously charged into the furnace by a Wellman charger. In

this way very rapid oxidation of impurities can be effected by oxidising slag, and considerable saving in time in the working of the charge is effected. The "mixers" used in the Bessemer *and open-hearth processes are simply large reservoirs of 300 to* 400 tons capacity, in which metal from a number of blast furnaces is stored and poured off by tilting as required. They are usually gas-fired, the air, if not the gas, being regeneratively heated. It is becoming more and more the general practice to use them as preliminary refining furnaces by the addition of suitable fluxes. Many of them are now basic-lined, and, by the formation of suitable slags, not only can the metal be desiliconised, but largely desulphurised. In this connection the **Saniter process** of desulphurisation may be mentioned. It is based on the use of calcium chloride in conjunction with lime, and is sometimes carried out *by placing in the mixer, before the molten iron is run in, a fusible* mixture of calcium chloride, lime, fluorspar, and limestone in certain proportions. As it melts and rises through the molten metal it removes a large part of the sulphur present. Its mode of action is obscure, but it seems probable that an oxychloride of lime is formed which enables a slag of great fluidity and basicity to be brought into intimate contact with the fluid metal.

An important feature in the construction of large modern furnaces is the insertion of a supplementary chamber between the "ports" of the furnace and the regenerators to act as a slag and "dust-catcher." This obviates the choking of the regenerators by the fluxing of the bricks, which might otherwise take place on account of the fine dust of iron ore or lime, a considerable amount of which is carried over mechanically with the gases in all open-hearth practice. Another important detail is the introduction of air-cooled hollow castings into the "block" of the furnace, which helps to prolong its life. In America the use of the Blair water-cooled block has effected considerable economy.

Three distinct methods of procedure in making open-hearth steel may be noted :—

(1) To work the charge of pig iron until it has reached the desired amount of carburisation, and then tap out.

(2) To completely decarburise the charge and add spiegeleisen or ferromanganese for recarburising.

(3) To completely decarburise the charge, and recarburise outside the furnace by the Darby or some similar process.

The first method is often adopted for steels containing 0·3 to 0·6 per cent. carbon, but for the best qualities the second method is preferred. For steels with 0·7 per cent. carbon and upwards

the third method is largely employed. In the **Darby process** free carbon is used for recarburising. Special carburising vessels were formerly employed, but afterwards found to be unnecessary, and now in similar processes it is customary to throw into the ladle at intervals a definite quantity of finely divided carbon. By this means a considerable saving of ferromanganese is effected. In adding the carbon there is no marked change in the other elements, and as the carbon is added to the charge in the ladle there is no reduction of phosphorus from the slag. The Darby process has this advantage over the ferromanganese process of recarburising in that, as there is a tendency for manganese to segregate in steel, a more uniform product is probable with the former process, especially for the higher carbon steels.

In order to overcome the difficulties of tapping large charges from the furnaces, "**Tilting Furnaces**" have been recently introduced. Of these the **Wellman** rolling-furnace is an example, in which the furnace is a strong steel shell lined with silica or magnesite bricks, resting on a pair of racks, and rolling on them by means of the segments of a large pinion. When pouring off slag or steel the furnace is rocked forward by means of two hydraulic cylinders mounted on trunnions at their lower ends, and having the upper ends of their piston rods attached to the pouring side.

Within the last few years several important modifications of the basic open-hearth process have been introduced, two of which are of sufficient practical importance to deserve separate mention—viz., the **Bertrand-Thiel** and the **Talbot** continuous process. In the former process as generally practised two open-hearth furnaces are used, preferably placed at different levels, so that the metal can easily be transferred from one to the other. Both are basic-lined. Either cold pig or molten metal from a mixer is charged into the first or "primary" furnace and largely dephosphorised and partially decarburised in the usual way. When the carbon is reduced to 1·5 or 2 per cent., and the phosphorus to about 0·2 per cent., it is transferred to the finishing furnace, in which scrap, oxide, and some lime have been previously heated, care being taken to keep back any phosphoric slag in the primary furnace. A vigorous reaction takes place, the non-metals being rapidly eliminated. By this process the time needed for working off a charge is considerably shortened, and the yield materially increased, especially when large tilting furnaces and molten iron are used.

The Talbot process involves the use of large basic-lined tilting furnaces of the Wellman type. Molten metal from a mixer is charged and converted into steel in the usual way; instead,

however, of pouring the whole charge, only one-third of the contents is teemed, and then a ladle of mixer metal equal in weight to that removed is poured into the bath of finished steel remaining in the furnace. Oxides and lime additions are made in the usual way with a Wellman charger, and when the metal is dephosphorised and decarburised to the required extent, another third is cast into ingots and more mixer metal charged into the furnace. In this way the furnace is worked continuously, being never less than two-thirds full of molten steel, and it is only emptied at the week-end. The chief advantages claimed for the process are a saving in fuel, an increase in output and yield, and a saving in charges for labour and furnace repairs.

A process which is still in its experimental stage, but which appears to be very promising, is the **Lash** process, in which steel is produced from the ore. It depends on the fact that when an intimate mixture of iron ore (such as magnetic iron sands), carbon, fluxes, and cast-iron borings (or granulated pig iron) is heated reduction readily takes place, and by suitably proportioning the mixture the desired grade of steel can be produced. The "Lash mixture" contains approximately :—

Granulated pig iron,	23 per cent.
Ore,	60 ,,
Coke,	11 ,,
Lime,	6 ,,
	100 ,,

A typical charge for producing 100 tons steel ingots in the open-hearth furnace is as follows :—

Lash mixture,	122 tons.
Pig iron,	32 ,,
Ore,	2 ,,

a certain amount of pig iron or scrap being used in addition to the Lash mixture.

The process is also being adapted to the electric furnace, in which case it is not necessary to use pig iron in addition to the mixture. For producing 100 tons steel the charge used is—

Lash mixture,	172 tons.
Ore,	2 ,,

A combination of the Bessemer and open-hearth processes has lately been practised under the name of the "**Duplex process.**" According to this method it is customary to blow the Bessemer heats until the carbon is reduced to about 1 or 1·5 per cent., the silicon and manganese, of course, having been previously

eliminated, and then to work off the remainder of the carbon together with the phosphorus and as much sulphur as possible in the open hearth.

Soft metal (ingot iron, "mild steel") is largely made by the Siemens process, and used for boiler and ship plates, bridge work, etc., while a harder grade, which may be reckoned as a true steel, is made for railway carriage wheel tyres. The following analyses show two grades commonly made :—

	Ingot Iron.	Tyre Steel.
	Per cent.	Per cent.
Carbon,	0·17	0·58
Silicon,	0·02	0·23
Manganese,	0·04	0·64
Phosphorus,	0·06	0·03
Sulphur,	0·01	0·03

PRODUCTION OF CEMENTATION STEEL.—For the production of the best classes of steel—*e.g.*, tool steel—none of the foregoing processes for making ingot iron or steel of moderate hardness is well adapted, on account of the impurities—*e.g.*, S and P—which the metal retains. Steel which is to be hardened for cutting purposes contains from 0·8 to 1·5 per cent. of C, and must be as nearly as possible free from other foreign constituents. In consequence, the very purest puddled bar is taken as the raw material and carburised, and thus converted into steel, by the **cementation process.** The bars of iron, which are about 3 inches wide and ¾ inch thick, and 8 to 10 feet long, are packed in firebrick boxes, set over a long grate, in furnaces commonly heated by solid fuel. The bars are packed in these chests in alternate layers with charcoal which has passed through a ½- to ¾-inch mesh sieve. Each chest is about 3 feet in depth, and takes a charge of 7 to 8 tons of iron. A thick layer of charcoal is placed on the top and covered with grinders' waste (siliceous and steely particles). The temperature of the furnace is kept at a bright red heat for seven to ten days, according to the content of carbon required in the finished steel, trial bars being withdrawn from time to time, and their quality judged by their fracture, which has become crystalline and lighter in colour than that of the wrought iron used as a raw material. When pure iron is heated with carbon, the latter is gradually absorbed and penetrates the mass of iron, converting it into steel. The maximum amount that can be absorbed is 5 per cent. The mechanism of the change is not yet understood. According to one view the carbon passes through

the iron in the form of gaseous compounds which are decomposed, giving up their carbon to the iron; possibly the gaseous compounds are decomposed at the surface and the combined carbon transmitted layer by layer. Whether the carbon diffuses as such in the same manner as a solid gradually diffuses in a solvent, or whether as carbides of iron, is still a matter which is under discussion.

When the bars are withdrawn they are found to be covered with blisters, which are due to the production of CO by the action of the carbon on enclosed particles of slag. The "blister steel" is irregular in texture, the content of carbon decreasing from the outside to the inside of the bars. It may be rendered homogeneous in one of two ways. Thus, the bars may be made into a bundle and welded, the product being known as "shear steel," and if then cut up and again welded, as "double-shear" steel. The second and better way to obtain a uniform product is by actual fusion in crucibles. Steel crucibles are made of refractory fireclay and plumbago, and hold from 60 to 90 lbs. The old coke-hole, practically the same as 100 years ago, is still largely used for heating the crucibles. This is merely a rectangular cavity 18 to 24 inches square and 3 to 4 feet deep. A number of such furnaces are arranged side by side. Comparatively recently gas-fired furnaces on the regenerative principle have been introduced, while the Nobel liquid fuel furnace is an arrangement for heating a number of crucibles with refined petroleum. Electric furnaces are also being employed for this purpose on the Continent, and in the future doubtless electric furnaces will be largely adopted for the manufacture of what is now known as "crucible steel," especially for dealing with comparatively large charges. Crucible steel is not only made from blister steel, but also from mixtures of the best Swedish iron recarburised in the pots by means of charcoal. Cheaper qualities are made in large quantities from selected steel scrap by melting this with Swedish pig iron or other recarburising material. The method of making cast steel by melting malleable scrap iron with charcoal and oxide of manganese introduced by Mushet in 1801 is still largely practised. Whatever the materials used, the molten steel is kept in the fire sufficiently long to eliminate gases and prevent blowholes. This is termed "killing." The use of aluminium is now becoming general in crucible steel manufacture as a substitute for "killing," it being found that the addition of very small quantities of this metal (0·02 to 0·03 per cent.) shortly before teeming has the same effect in producing sound castings. The metal is cast into ingots, and is known as "crucible cast steel," which needs reheating and hammering before it is fit for

use in tool-making. The following analysis shows the composition of a good tool steel :—

Carbon,	1·14
Silicon,	0·17
Manganese,	0·10
Sulphur,	Nil.
Phosphorus,	Nil.

MALLEABLE CAST IRON.—The process of removing carbon from cast iron at a temperature below its melting point, by heating it with a solid oxidant, may be regarded as complementary to that of imparting carbon to wrought iron in the manufacture of steel by the cementation process (*v.s.*). The process of preparing malleable cast iron was formerly thought to be an example of this reaction. In this process castings of white iron containing but little silicon and manganese are packed in firebrick boxes or in cast-iron crucibles in powdered hæmatite, gradually raised to a red heat, kept at that temperature for about three days, and allowed slowly to cool. The metal is malleable so that it can be forged hot.

The rationale of the process is somewhat obscure, but it appears that the carbon is eliminated by oxidation while still in combination with the iron, by direct reaction with the oxidising medium. At a moderately high temperature (above the recalescence point Ar_1, see p. 215) iron carbide begins to decompose, and the released carbon is dissolved in the iron until an equilibrium stage is reached, at which the pressure of the dissolved carbon prevents the further dissociation of the carbide. The carbon now in solution diffuses outwardly to the surface to replace the carbon already eliminated. In this way an external layer of decarburised iron is formed, which may attain considerable thickness. Malleable castings can also be made from white iron by heating in a non-oxidising mixture, in which case the combined carbon is largely converted into the graphitic state without appreciable loss. The process is said to be more rapid and better suited for larger articles, and is the one chiefly followed in the United States. Such malleable cast iron is known as "blackheart," from the black, velvety appearance of its fracture. It appears that as the temperature rises the solvent power of iron for carbon increases until at 1,030° C. it can dissolve 1·5 per cent. At this critical temperature, however, the whole of the residual carbide decomposes in spite of the carbon pressure around. The iron cannot, however, dissolve more than 1·5 per cent. at this point, and the remainder of the carbon is, therefore, deposited as graphite as fast as it is separated.

CASE-HARDENING.—Another instance of the transference of carbon to iron from without, in the manner occurring in the cementation process, is afforded by the operation known as case-hardening. This is best carried out by heating the iron to be case-hardened in a bed of charred organic matter—such as is nitrogenous—*e.g.*, leather, bone dust, etc., being usually adopted. By this means a layer of steel, which may be as much as $\frac{1}{16}$ inch in thickness, is formed on the outside of the article treated. A slighter steel film may be obtained by sprinkling the red-hot metal with powdered potassium ferrocyanide. Armour plates for battle ships are externally hardened in this way.

Harvey's process consists in carburising one side of a mild steel plate by cementation, the carburised face being afterwards hardened by sudden chilling from a red heat. Another important process for armour plates is that of Krupp, of Essen, who carburises by means of gaseous hydrocarbons, and then hardens. Two plates are placed on a hearth, one above the other, with a space between, and with their faces inwards, so that the carburising gases may pass between them. A process for making compound armour plate, and avoiding the tedious process of cementation, is that of Beardmore, of Glasgow, who produces ingots composed of layers of hard and soft steel perfectly united. A layer of steel is run into a horizontal mould, the bottom of which is kept cool, which causes the bottom layer of steel to set quickly; while the upper layer is still liquid, a charge of milder steel is poured in, and unites with it, and so on with a third layer of still softer metal. The ingots are pressed and rolled into plates. By this means a much greater depth of hard steel can be obtained in a comparatively short time than is possible by a cementation process such as Harvey's or Krupp's.

As regards the material now used for armour plates, it is generally a special steel with varying percentages of such metals as nickel, chromium, manganese, vanadium, and tungsten.

EFFECT OF FOREIGN ELEMENTS UPON IRON AND STEEL.—The purest iron attainable is that prepared by electrolysis. The best conditions for obtaining it are said to be as follows:—The bath consists of a solution of 200 grammes of ferrous chloride (or ferrous ammonium sulphate), 50 grammes magnesium sulphate, and 5 grammes sodium bicarbonate per litre; this solution is electrolysed with a current density of 0·003 ampere per square cm. at the cathode, which consists of copper thinly silvered and iodised and maintained in rotation. The anode is of wrought iron. More sodium bicarbonate is added as electrolysis proceeds. The iron deposited improves in quality as the

process proceeds, and finally reaches a strength of over 30 tons per square inch. Owing to the low current density, the iron is free from hydrogen, which is always present when high current density is used. The amount of hydrogen thus combined may amount to 240 to 250 times the volume of the iron, corresponding with the formula $Fe_{13}H_2$. This form of iron containing hydrogen is hard and brittle, whence its application in facing copper plates used for electrotype printing processes; the method of depositing steel-like iron for this purpose is known as *aciertype*. The Langbein-Pfanhauser-Werke Aktiengesellschaft of Leipzig is now producing on a commercial scale plates and other articles of iron of at least 99·95 per cent. purity. The process is due to F. Fischer, and the iron is obtained electrolytically in a single operation from the electrolytic bath, using merchant iron as the anode. As would be expected, such pure iron possesses extraordinary softness and ductility, its hardness, as determined by Brinell's method being 92 before and 62 after annealing (on the same scale annealed copper = 95 and aluminium = 52). Pure iron has a specific gravity of 7·86, but this depends somewhat on the mechanical treatment to which it has been subjected, for when stressed its specific gravity is lowered. The maximum value may be taken as about 8·0.

According to Carpenter and Keeling, pure iron (containing 0·01 per cent. carbon) melts at 1,505° C. When allowed to cool from this temperature, the regularity of cooling is interrupted at three different temperatures, an evolution of heat taking place which prolongs the period required for the metal to cool through a given range of temperature. The temperatures at which retardation during cooling (*refroidissement*) takes place are indicated by the symbols (introduced by Osmond) Ar_1, Ar_2, Ar_3. Three similar arrests are noted in the rate of heating as the temperature is raised from that of the atmosphere to the melting point of iron, the points observed during heating (*chauffant*) being denoted by Ac_1, Ac_2, Ac_3. The points recorded with a falling temperature are about 30° C. lower than the corresponding points recorded with a rising temperature. The symbols Ar_1 and Ac_1, therefore, refer to the same physical change, any difference being merely due to the direction from which we approach the transition point. The three points are approximately 870° C. (1,598° F.), 760° C. (1,400° F.), and 680° C. (1,256° F.). These changes are not equally well marked in all varieties of iron and steel, the nature and proportion of other elements present influencing both the number and position of the points of arrest. With the purest iron obtainable, the lowest point is scarcely perceptible, while the highest point is most distinct. On adding

more and more carbon the highest point is caused to fall steadily, until with high carbon steels only one point is noted; this is extremely well marked (674° C.), so much so as to cause the steel, after it has cooled to a dull red heat suddenly to glow *again and increase in length. This phenomenon is known as* **recalescence.***

As an explanation of the above facts, Osmond has advanced an **allotropic theory,** according to which iron is capable of existing in three modifications, known respectively as α, β, and γ-iron. The last form is stable above 870° C. (A_3), and is usually formed on the solidification of the fused metal. Between Ar_2 and Ar_3 the β form is the most stable, while the α modification is produced if the iron is slowly cooled below Ar_1, and is the form *which is capable of assuming magnetic properties.*

Iron is peculiarly sensitive to the influence of impurities, which may also affect the influence of each other. The impurities most commonly present in cast iron, wrought iron, ingot iron, and steel are C, Si, S, Mn, and P. As will be seen by reference to the analyses of various grades of iron already quoted, cast iron contains each of these elements in the largest proportion, including those which have a deteriorating effect. It is on account of this that cast iron is a comparatively weak and brittle *material. The weakness is largely due, in grey and mottled* cast iron, to scales of graphite disseminated through the metal, thus destroying its perfect continuity. When, from the absence of silicon (*v.s.*), white cast iron is produced, it is still of low strength from the effect of the sulphur and phosphorus which it contains, although their action cannot be definitely attributed to the same cause, but rather to a more subtle influence indicated below. In the best wrought iron, ingot iron and steel, the quantities of S and P are reduced to a minimum, for when present in appreciable amount—as in the case of puddled iron—they only exist as constituents of interstitial slag.

In considering the effect of impurities on steel, the unequal distribution of such impurities is of the greatest importance. *This unevenness is due to the tendency of certain constituents* to segregate, especially when the steel is slowly cooled. Howe divides bodies which tend to segregate into three groups—(*a*) compounds which differ from the rest in fusibility, (*b*) compounds which have a strong affinity for each other, (*c*) compounds which differ greatly in density from the rest of the mass. *For instance,* carbon and phosphorus have a greater affinity for iron than manganese, and the carbides, phosphides, and sulphides of iron

* A fourth recalescence in steel containing 0·2 per cent. carbon has been observed recently by Arnold (*Brit. Assoc.*, Sept. 1910).

are comparatively fusible and of low density. According to Harbord, sulphur and phosphorus are the elements most unequally distributed, but carbon also segregates very readily. It is generally found that segregation of one impurity induces segregation of the rest. While chrome and tungsten steels are very liable to segregation, nickel steels are remarkable for their uniformity.

Carbon is by far the most important of the foreign elements present in commercial iron. The graphite which occurs in grey cast iron is rarely found in wrought iron, ingot iron, or steel. According to Ledebur, carbon, in a state similar to but not identical with graphite, may be formed by prolonged heating of iron containing the forms of carbon next to be mentioned. The existence of this form of carbon (called "temper carbon") is, however, not generally accepted. On the relations of these two remaining forms of carbon ("hardening carbon" and "cement carbon") the explanation of the phenomena of hardening, tempering, and annealing largely depends. It is this capability of being hardened, tempered, and annealed which constitutes the essential difference between steel and wrought or ingot iron, and it first becomes evident when the proportion of carbon exceeds 0·25 per cent. It must be understood that this statement applies to iron containing carbon and no other impurity, as other elements—*e.g.*, phosphorus or sulphur—may exhibit analogous properties with a lower percentage of carbon. The hardening effect of these cannot be substituted for that of carbon, as the former gives "cold-short" iron—*i.e.*, a metal which is brittle (especially to shock)—and the latter "red-short" iron—viz., one which is brittle at a red heat and cannot be worked.

In the following description of the process of hardening, true steel, consisting of iron with more than 0·25 per cent. of C and a minimum quantity of other elements, will be spoken of. On heating steel above the critical point Ar_3 (about 870° C.), and cooling it suddenly—*e.g.*, by plunging it into water—it will be rendered hard, whereas if allowed to cool slowly from this temperature it is comparatively soft. Such process of hardening is always adopted for steel tools—*i.e.*, those capable of taking and retaining a cutting edge. It is obvious that as the steel after hardening cannot be worked except by grinding, the tool must have received its shape before hardening, so that nothing remains but to grind it to an edge. But few tools can be used in as hard and brittle a condition as that obtained by direct quenching from a red heat in cold water. The excessive hardness must be removed by *tempering* in order that the edge of the tool may not

be easily chipped but may possess a certain elasticity or springiness. The process consists in gradually reheating the hardened steel to a temperature, considerably short of redness, proper to the particular class of tool to be prepared, and quenching in water when this is reached. These temperatures are indicated by various colorations of the bright steel surface, and may be stated as follows:—

Coloration.	Temperature	Class of Tool
Faint yellow,	220° C. = 428° F.	Surgical instruments.
Straw yellow,	230° C. = 446° F.	Razors.
Full yellow,	243° C. = 469° F.	Penknives.
Brownish-yellow,	255° C. = 491° F.	Chisels and shears.
Brown,	265° C. = 509° F.	Axes and plane irons.
Purple,	277° C. = 531° F.	Table knives.
Bright blue,	288° C. = 550° F.	Swords and springs.
Blackish blue,	316° C. = 601° F.	Hand saws.
Black,	400° C. = 752° F.	Spiral springs.

It is found that unless steel be heated above the critical temperature Ar_3 it cannot be hardened by quenching, nor is it hardened if it be cooled slowly from this temperature ("annealed"). It is obvious that inasmuch as there can be various grades of rapidity of quenching (*e.g.*, by the use of mercury, cold water, hot water, and hot oil) the hardening of steel may be more or less perfect, and it is possible, by limiting the hardening in this way, to attain a given degree of hardness or "temper" by a single operation.

When hardened steel is dissolved in dilute hydrochloric or sulphuric acid, nearly the whole of its carbon is evolved as hydrocarbons. When fully annealed, the carbon is left, on dissolution of the steel in the same acids, in a form apparently combined with iron as a carbide, corresponding with the formula Fe_3C. Hardened steel that has been "tempered" or "let down," or steel that has been imperfectly hardened contains carbon in both forms. The distinction, already mentioned, has thus arisen between hardening carbon and cement carbon. The former appears to form with the steel a solidified solution, while the latter is diffused through the metal as grey scales, both conditions being recognisable in the fracture of the metal.

The mixture of Fe_3C (cementite) and pure iron (ferrite) is

* These figures are only of limited significance, because it has been found that prolonged exposure to a lower temperature will produce the same colour as will a short exposure to a higher temperature.

known as "pearlite," and by means of the microscope is seen to occur in two forms—the lamellar and the granular. The former, made up of very thin plates, is found in annealed steel, while the granular variety is found in steels which have been reheated to a low temperature. Pearlite appears to be practically the sole constituent of unhardened steel containing from 0·8 to 0·9 per cent. of carbon. The characteristic constituent of steels quenched from a high temperature is "Martensite," a solid solution of carbon in iron, which appears under the microscope like a system of interlacing fibres.

From the consideration of the above it will be seen that the constitution of steel may be viewed from two distinct standpoints, one of which is concerned with the molecular changes occurring in the iron itself, while the other has for its object the study of the relations of iron to carbon and the other elements. These two views are known as the "*allotropic*" and "*carbon*" theories respectively. The former, involving the acceptance of three allotropic modifications of iron, has been briefly outlined above (p. 216). According to this theory, the evolution of heat at the critical points Ar_3 and Ar_2 is caused by the passage of iron from the γ to β and from the β to α states respectively, any carbon present being diffused in the different modifications of iron. The evolution of heat at Ar_1 is caused by the combination of carbon with α-iron to form Fe_3C as "cement carbon." In the passage of iron from the β to α state at the point Ar_2 the steel becomes magnetic. The cause of hardening is said to be the retention by sudden cooling of the hard γ and β forms of iron, which retention is aided by the presence of carbon.

The "*carbon*" theory, on the other hand, endeavours to explain the above phenomena by changes in the condition of the carbon alone. Above the critical point Ar_1 steel is supposed to consist of iron and hardening carbon (possibly as a solid solution). The evolution of heat at the point Ar_1 is then caused by the passage of hardening carbon to the cement state, steel below this point consisting of iron and cement carbon combined as Fe_3C. The phenomenon of hardening is ascribed to the retention by sudden cooling of the carbon in its hardening state. The older carbon theory has no explanation to offer with regard to the critical points Ar_2 and Ar_3. Prof. Arnold has, however, since developed a "*sub-carbide*" theory, which offers a fuller explanation of these facts. According to this theory the critical point Ar_3 marks the formation of an intensely hard sub-carbide of iron $Fe_{24}C$, which remains unaltered if the metal be suddenly cooled, and the retention of which is the cause of hardening. At the point Ar_2 the evolution of heat is supposed to be due to the passage of iron

from a plastic to a crystalline condition, while at Ar_1 the sub-carbide $Fe_{24}C$ dissociates with formation of Fe_3C. It will be noticed that in both the allotropic and carbon theories the lowest critical point Ar_1 is regarded as due to the formation of Fe_3C.

Both schools of metallurgists agree in regarding carbon as an essential constituent of steel, the properties of which are determined by the amount and condition of this element; the "allotropists," however, further contend that the condition of this carbon is itself fixed by the allotropic condition of the iron with which it occurs.

The allotropic theory has recently been extended by including in it what is known as the "*solution theory*," which affirms that carburised iron when fluid is a solution of carbon in iron, and that under certain conditions the solidified mass also forms a solid solution. These solutions obey the ordinary laws of solution, which can be used, therefore, to explain both the mode of solidification and the molecular changes that take place after solidification. The full development of the theory is too abstruse a subject to be dealt with in these pages.

The following are the most important constituents of steel, which have been recognised chiefly by means of the microscope :—

Ferrite, or pure iron, occurs in trimorphic crystals with polygonal or rounded boundary lines produced by the interference of cubes or octahedra forming from a series of centres.

Pearlite is a definite mixture of metallic iron and iron carbide Fe_3C (cementite) forming the eutectoid. It contains 0·89 per cent. of carbon or 13 per cent, of Fe_3C, the carbon being molecularly associated with only about 12 per cent. of the iron, 87 per cent. of the latter being in the free state.

Hardenite.—According to Arnold, this also contains 0·89 per cent. of carbon, but in this case it is associated with 99 per cent. of the iron. It is found in quenched steels.

Austenite is a solid solution of carbon in γ-iron, and is produced by quenching steels above the Ar_{3-2-1} changes.

Martensite is a solid solution of carbon in β-iron, and is produced by quenching steels just below the Ar_3 change.

Troostite is considered to be a solid solution of carbon in α-iron, and produced by quenching steels just below the Ar_2 change.

Sorbite is an emulsified form of pearlite, in which the cementite (Fe_3C) has not had time to segregate. It is formed by rapidly cooling steel immediately below the Ar_1 change.

Sulphide of iron is described by Arnold as occurring in masses or as a mesh work in manganese-free steel.

Sulphide of manganese is frequently present in steels as globules or cigar-shaped masses of a dull grey colour.

Phosphide of iron was *observed by Stead in 1900, and with free iron forms an eutectic similar to pearlite.*

Silicate of manganese *is often present in steels, sometimes visible* to the naked eye, and at other *times only under the microscope.*

Oxide of iron is *often present* in *commercial steels.*

It has been already mentioned that elements other than carbon influence both the number and position of the critical points of iron, and they will also influence the corresponding changes in the allotropic forms of the iron. Thus, iron containing small proportions of manganese shows a retardation at a point rather below the point of arrest for carbon steel and when the quantity is increased to 7 per cent. a material (manganese steel) is obtained in which the iron appears to exist in the γ condition and to be consequently hard. **Manganese steel,** which is the name applied to alloys of iron and manganese containing 7 to 14 per cent. Mn, is extremely tough and hard, on which account it has found but few applications, as it cannot be worked in the same way as hard carbon steel by annealing, machining, and re-hardening. Manganese steel containing 12 to 14 per cent. Mn possesses, however, the peculiar advantage of being softened and toughened by the following treatment:— When heated to 990° to 1,090° C., and plunged into cold water, it becomes sufficiently soft to be machined. Hardness may then be restored by reheating to a bright red and cooling in air. Manganese steel is non-magnetic, has a high electrical resistance, and a low coefficient of expansion : it has a high tensile strength and elongation, is self-hardening, and is largely used for making such things as jaws of rock breakers, dredger buckets, and switches and crossings, where both hardness and toughness are necessary.

The influence of nickel is somewhat similar to that of manganese on steel, in that small proportions, up to 5 per cent., increase the hardness and toughness of the product, and larger proportions, 21 per cent. and over, form with the iron an alloy of characteristic properties. Thus, nickel steel with 21 per cent. of nickel is non-magnetic at the ordinary temperature, and is, therefore, considered to contain iron in the γ or β state, and has a low coefficient of expansion and low electrical conductivity, but becomes magnetic on cooling strongly in a mixture of solid CO_2 and ether (− 79° C. = − 110° F.). See also under *Nickel*, p. 27.

A brief account of other special steels has been given in Chapter I. (p. 21). With regard to chromium steel, it may be remarked that in small quantities this element slightly raises the tensile strength of steel, and in large quantities the brittleness, both effects being modified by the amount of carbon present. Steel for projectiles usually contains 2 to 3 per cent. Cr and 1 per

cent. carbon. Steel containing both nickel (2 per cent.) and chromium (1 per cent.) with about 0·4 per cent. carbon is also used for armour-piercing shells. The nickel toughens while the chromium and carbon harden the steel.

Tungsten and molybdenum steels are used for self-hardening cutting tools and for magnets. These elements prevent the softening effect of the increase of temperature of the tool. The wearing properties of ordinary tool steel are improved by the addition of a small percentage of tungsten, while a first-class tool steel may contain 7 per cent. tungsten and 1 per cent. carbon. Mushet steel contains 5 to 8 per cent. tungsten and about 2 per cent. carbon.

Special alloy steels, known as air-hardening steels and high-speed tool steels, which are revolutionising our machine shops, contain alloys of tungsten-chromium, or chromium molybdenum, and are largely made in the crucible by melting suitable mixtures. The resistance of these steels increases with rise of temperature. They contain from 0·75 to 3 per cent. Cr, 4 to 8 per cent. W, and 4 per cent. Mo, the latter being used for working hard steel. The carbon is usually less than 1 per cent.

Vanadium exerts a more powerful influence on steel than any of the above metals. Its effect is similar to that of nickel in increasing the tensile strength and elastic limit, but is much more efficient, 0·2 per cent. producing the same effect as 3 to 4 per cent. Ni. It is supposed that vanadium prevents segregation, and promotes the uniform distribution of carbon by forming a double carbide of iron and vanadium, and in this way removes a cause of brittleness due to vibration. Much of the success of the motor industry is due to the use of these special alloy steels for parts subject to vibratory and alternating stresses. The addition of aluminium to steel to produce soundness in the ingots has already been noticed (pp. 21, 207).

Attention has recently been drawn to the influence of **titanium** on steel, more especially on steel rails. The addition in the ladle, after ferromanganese or ferrosilicon, of 0·5 to 1·0 per cent. ferrotitanium (containing 10 to 15 per cent. Ti) is said greatly to improve the quality of the steel. It probably does this by combining with the last traces of oxygen and also with any nitrogen in the steel, thus making it more homogeneous. The tensile strength of such a steel is stated to be from 60 to 75 per cent. higher than that of ordinary Bessemer steel (see p. 207).

The ferro-alloys used for introducing these foreign elements are produced in the blast furnace by the reduction of ores rich in these elements (p. 191). The electric furnace is used also now for this purpose.

The grades of ordinary carbon steel most generally used, range

form 0·2 per cent. C (practically an ingot iron) to 1·5 per cent. C (a razor steel). Thus, boiler plates, ship plates, and bridge members will contain 0·2 per cent. ; rails, 0·35 to 0·45 per cent. ; tyres and guns, about 0·5 per cent. ; armour plates, 0·7 to 0·8 per cent. ; projectiles, 0·8 to 1·0 per cent. ; tool steel, 1 to 1·2 per cent. ; razor steel, 1·5 per cent. ; and draw-plate steel, 2 to 3 per cent. C. The simultaneous presence of 0·5 per cent. Mn may be taken as raising the grade of steel equivalently to an additional 0·1 per cent. C.

Apart from the effect on steel of the condition of the iron and of the carbon, is the influence of the actual crystalline structure of the metal. Other things being equal, a steel with a coarse crystalline structure is weaker than a steel with a fine structure. Overheating steel, or heating it considerably above its critical point, causes it to assume a coarse structure whatever the rate of cooling. This crystalline structure can be broken down by forging the hot steel, a plan adopted for heavy guns.

The mechanical effect of hardening steel is shown (1) by its change in specific gravity—*e.g.*, 7·9 before hardening, and 7·6 afterwards—the dilatation being about 5 per cent. ; (2) by its increase in tensile strength—*e.g.*, for a steel containing 0·8 per cent. C, 64 tons per square inch when hardened, in place of 44 tons when unhardened ; (3) decrease of ductility—for the same steel, an extension of 8 per cent. of its length when unhardened, and 1 per cent. when hardened. The same effect on tensile strength and ductility that is produced by hardening (quenching) can be obtained by subjecting the metal to severe mechanical stress, such as occurs in wire drawing. Steel wire, although not hardened by quenching, may have a tensile strength exceeding that of steel of the same grade that has been purposely hardened. This hardness, like that due to quenching, is removed by annealing.

The influence of impurities on steel has been referred to the relation between the atomic volume of iron and that of its associated elements. The following table shows that the ordinary impurities may be divided into two groups, according as their atomic volume is below or above that of iron (7·2) :—

	I. Atomic Volume.		II. Atomic Volume.
C, ...	3·6	Cr, ...	7·7
B, ...	4·1	W, ...	9·6
Ni, ...	6·7	Si, ...	11·2
Mn, ...	6·9	As, ...	13·2
Cu, ...	7·1	P, ...	13·5
		S, ...	15·7

The elements in the first series are believed to favour the retention of iron in the β state, and tend to the production of a hard metal; those in the second series are supposed to hinder the formation of β iron, and yield a softer, more ductile material. *This view is not strictly in accord with the known influence of several of the elements in series II., notably S and P (v.s.).*

ELECTROMETALLURGY OF IRON AND STEEL.

Electric energy has many advantages for the supply of heat in such metallurgical operations as are carried out on a moderate scale, the more obvious of them being its readiness of transit, control, application, the absence of ash, dust, and smoke, and the wide range of temperature which is possible. The early progress in the electrometallurgical production of iron and steel was slow, probably because the efforts of the pioneers were directed amiss. *In the first place, it is well to distinguish clearly between (1) electric reduction of iron ores, and (2) electric refining, or production of steel and ferro-alloys.* The ambition of the pioneers was to smelt iron electrically from its ores. This can and has been accomplished, but it is usually more costly than the production of steel and alloys of iron by electrical means, using as raw material the ordinary products of the blast furnace, inasmuch as electrical energy is commonly dearer than energy obtained direct from fuel. Electric processes must necessarily be considered in competition with existing methods. The blast furnace effects the required reduction of the ore in a simple manner. Moreover, especially with the modern tendency to utilise the waste gases, it is a fairly efficient thermal device, and as it uses fuel direct instead of in a round-about electrical manner, it is difficult to displace except in those places where fuel is extravagantly dear, whereas in the conversion of cheap pig iron into high-priced steel or special iron alloys the cost of energy necessary for the process is not so large a part of the total cost as to make electrical methods impracticable.

The conditions in this country are such that the electric furnace cannot compete with the blast furnace, and the direct smelting of iron ore is of less practical importance than in countries like Sweden and Canada, which possess large ore deposits, cheap water power, and in which fuel is comparatively dear.

Electric Smelting of Iron Ores.—The simplest form of furnace for this purpose is vat-shaped with a carbon block built into the sole of the furnace, *and an adjustable vertical electrode suspended above the top of the furnace* by suitable gear. The ore mixed with the necessary amount of reducing agent and suitable fluxes

is fed into the furnace at the top, and an arc is struck between the two electrodes. The mixture gradually melts and forms a fused bath, the resistance of which gives rise to sufficient heat to effect the reduction and fusion of the metallic iron. The upper electrode is gradually raised as the iron collects, and the latter is tapped at intervals. A modified form of furnace of this type has been designed by Messrs. Keller & Co., whose process, as carried out at Livet, was reported on favourably by the Commission appointed by the Canadian Government in 1904. Under certain favourable conditions as to cost of electric energy pig iron of all grades can be produced commercially at quite a reasonable cost in this furnace, a diagrammatic figure of which is shown in Fig. 19.

It consists, preferably, of four hearths arranged in two pairs, in series, the members of each pair being in parallel, and grouped in such a way that as the metal is reduced it collects in a central well, where it is kept hot by a subsidiary electrode. By the insertion of carbon blocks into the sole of each furnace, and connected by copper bars, an alternative path for the current is provided to act as a shunt when the hearths are in turn emptied, thus enabling the furnace to be worked continuously without very greatly varying the load on the alternator.

In 1906 the Canadian Commission carried out experiments at Sault Ste. Marie, Ontario, to ascertain whether Canadian magnetites and certain ores existing in large quantities and containing considerable quantities of sulphur, but no manganese, could be smelted to produce high-class pig iron ; also if charcoal and peat-coke could be used as the reducing agent. The experiments showed that such ores can be readily smelted, that low sulphur pig iron can be obtained from high sulphur ores, and that charcoal, even of inferior quality, can be satisfactorily used as a reducing agent without briquetting. Moreover, a pig iron of good quality containing only 0·40 per cent. titanium can be obtained from titaniferous iron ores containing as much as 17 per cent. TiO_2. This last point is very important, as it makes available all the titaniferous iron sands of the St. Lawrence district and of New Zealand, which are quite unsuitable for use in the blast furnace. The recommendations in the above report have been made use of in the design of the Swedish furnace by Messrs. Grönwall & Lindblad, of Ludvika (The Electro Metal Company), an installation of which is now being built in Norway for the electric production of pig iron. The furnace is shown in section in Fig. 20.

It is really a combination blast furnace and electric furnace design. A vertical shaft supported on columns is superimposed

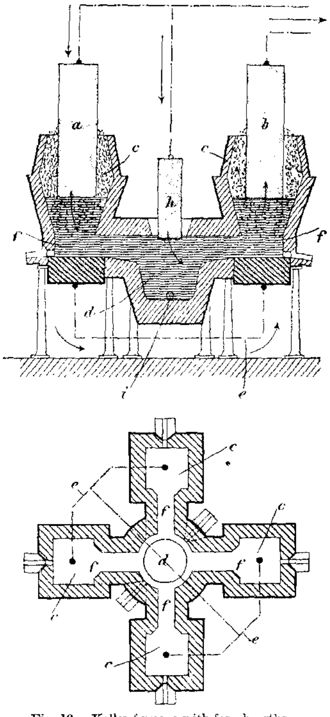


Fig. 19.—Keller furnace with four hearths.

upon, and opens into, a large smelting chamber at the bottom. The latter is so proportioned as to provide a considerable amount

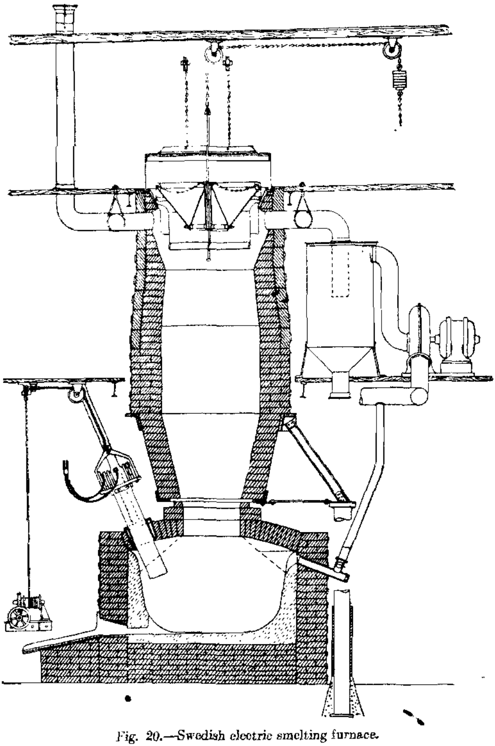


Fig. 20.—Swedish electric smelting furnace.

of free space between the charge and the arched roof, through which the three carbon electrodes (one of which is shown) project into the charge. The gaseous products of reaction leave the furnace at the top, and are blown back through tuyeres into the lower smelting chamber, the object being to cool the roof of the furnace chamber above the electrodes. It is essential to keep this brickwork as cool as possible, otherwise it is destroyed and becomes a conductor of electricity, giving rise to a short circuit. The ore, fuel, and flux, crushed to a suitable size, are fed through a hopper, the ore being partially reduced by the carbon monoxide rising through the charge, and reduction completed in the smelting chamber. No air is used in the process, and the gases are produced from the carbon in the fuel, and the oxygen in the ores :—

$$FeO + C = Fe + CO.$$

The temperature of the escaping gases is generally low, and they contain CO_2 (8 to 41 per cent.), CO (40 to 60 per cent.), and steam, but no nitrogen.

A somewhat similar electric pig-iron furnace is being used by the Noble Electric Steel Company in California.

The **Stassano furnace** is one of the oldest of the electric furnaces for the smelting of iron ores. It is an arc furnace in which the necessary heat is obtained by direct radiation from the arc, and from the roof and sides of the furnace.

A modern form of the furnace is illustrated in the accompanying diagrams. It rotates on an axis inclined about 7° to the vertical, in order to give a mixing action to the molten materials on the hearth, and is hermetically closed to ensure a neutral atmosphere. The three carbon electrodes, which are water-cooled, are supplied with three-phase alternating current, and revolve with the hearth, the electrical contacts being arranged for by sliding brushes. The furnace is lined with magnesite blocks. Only the very purest hæmatites, such as exist in Northern Italy (where the process is worked), are smelted, and these are ground very fine, and made into briquettes with carefully adjusted proportions of carbon and flux. The reduction is effected entirely by the solid carbon. It is claimed that by adjusting the proportions of pure ore, carbon and flux, steel of any required grade can be produced direct from the ore. In its present form the furnace is unsuitable for smelting impure ores, but it is being used successfully for refining purposes.

As regards the energy required for electric smelting, experiments have shown that a ton of pig can be produced with

a consumption of about 1,700 kilowatt hours. Apart from the question of energy, the electric-smelting furnace has certain distinct advantages. Thus, whereas the blast furnace must be large, generally 90 feet in height, electric furnaces may be very

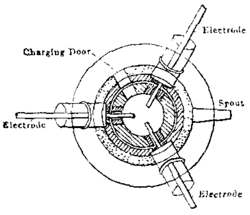


Fig. 21.—Transverse section A-A.

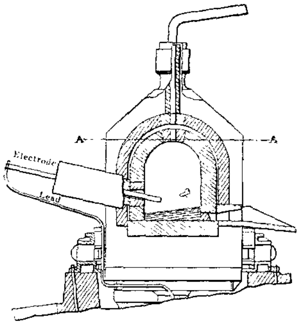


Fig. 22.—Stassano furnace.

much smaller. Consequently, repairs are more easily effected, and it is not such a serious matter if the charge is not correct, or if the furnace has to be shut down; moreover, regulation of the temperature is more easy.

ELECTRIC REFINING PROCESSES—PRODUCTION OF STEEL.

These processes are not really electric; electricity is used in them solely as a source of heat, and the purification is brought about by the same means to which we have become accustomed in the puddling Bessemer and open-hearth processes. In fact, for all practical purposes the electric furnace is a closed basic "open-hearth" furnace, in which the temperature is much higher, and which possesses the great advantage that the heat can be supplied without the simultaneous introduction of oxygen. Carbon, silicon, and phosphorus are removed chiefly by oxidation with iron oxide, and sulphur is removed in part as sulphide of manganese, which distributes itself between metal and slag, and partly as calcium sulphide, which apparently passes entirely into the slag. Electric furnaces are of great variety of size and form, but they may be classified conveniently under three heads—(1) arc furnaces, (2) resistance furnaces, and (3) induction furnaces.

Arc Furnaces.—The best known furnace of this type is the Stassano furnace, which we have already described (p. 228). When used for the manufacture of steel from a mixture of pig iron and scrap, iron ore is added in the usual way to oxidise the impurities, and lime to form a basic slag. The furnace is also largely used for refining steel from the Bessemer or other process.

Resistance Furnaces.—This is the type of furnace most commonly employed, in which the heat is produced by the resistance to the passage of the current which is offered by the substance which is to be heated. A familiar example of this type of furnace is that introduced by Héroult, and which has been in successful operation for several years at La Praz in France, Kortfors in Sweden, in Canada, and elsewhere. The construction of the furnace may be seen from Fig. 23.

Essentially it is a tilting furnace, very similar to that of Wellman (*q.v.*), through the arched roof of which two large water-jacketed carbon electrodes depend. The current passes from one of these through a short air gap, to the bath of metal, and from the bath of metal through a second short gap to the other electrode, and can be regulated either by adjusting the position of the electrodes by hand or automatically, according to the variation of voltage between each electrode and the bath. The furnace is, as usual, basic-lined, and the section of the roof between the electrodes is commonly made of bronze, in order that no magnetic circuit may surround them. At La Praz an alternating current of 4,000 amperes and 110 volts is used. The furnace is

especially useful for converting common steel scrap of average quality into steel of the highest quality. In a recent paper on "Electric Smelting" read before the West of Scotland Iron and Steel Institute, F. W. Harbord thus describes the method of working :—"Miscellaneous scrap, with some lime, is charged on the furnace hearth, and as the charge melts, further additions of scrap and lime are made, a little pure iron ore being added when the metal is entirely melted. After the bath has been molten for some time the furnace is tilted, the slag poured off, and finally raked off the surface, until practically nothing but metal remains in the furnace. A new slag is now formed by suitable additions of ore and lime ; this is melted and kept in the furnace for some time, when it is removed in the same way as the first slag, and a third slag formed to remove the last traces of impurity. Ferro-silicon and ferromanganese in the case of low carbon steels is

A A, Working doors.
B C, Magnesite bottom.
E, Entering electrode.
F, Exit electrode.
G, Molten slag.
H, Molten metal.
J, Pouring spout.
K L, Trunnions.
M N, Outer brickwork.

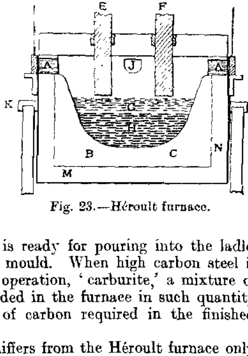


Fig. 23.—Héroult furnace.

now added, and the metal is ready for pouring into the ladle, and teeming into the ingot mould. When high carbon steel is required at the end of the operation, 'carburite,' a mixture of pure iron and carbon, is added in the furnace in such quantity as to give the percentage of carbon required in the finished steel."

The Keller steel furnace differs from the Héroult furnace only in mechanical details. The process is practically the same.

More recent examples of resistance furnaces are the Girod and Giffre furnaces, which may be described as bottom-electrode furnaces. The former, which is being used successfully at the Ochler Works, Aaran, Switzerland, is a tilting furnace very similar in construction to the Héroult furnace (see Fig. 23). The two electrodes passing through the roof are, however, of like polarity, while the molten metal, which is in contact with soft

steel pole pieces embedded in the hearth, forms the negative electrode.

The lower ends of the negative pole pieces are water-cooled. The usual charge consists of steel and cast-iron scrap and turnings with some pig iron, lime being also added as a flux. The characteristic feature of the Giffre furnace, an illustration of which is given, is that only one of the electrodes passes through the roof of the furnace into the hearth, the other electrode being contained in a separate chamber built on to the main body of the furnace, the electrical connection being maintained by a narrow

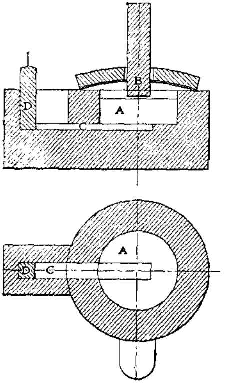


Fig. 24.—Giffre furnace.

A, Molten steel; B, upper electrode; C, molten steel connecting with lower electrode; *D*, *lower electrode*.

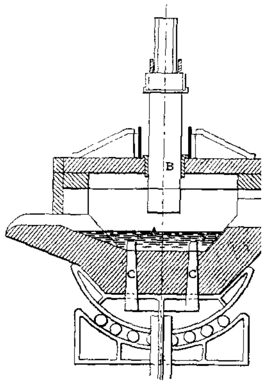


Fig. 25.—Girod furnace.

A, Molten metal; B, upper electrode; C, lower electrode.

channel of molten metal. The furnace would, therefore, appear to be structurally stronger than the Héroult type, and to be practically free from any danger of short circuiting between the electrodes. It is being successfully used for the manufacture of low carbon ferro-alloys.

Overhead electrode furnaces of the Héroult type have the

defect of having violent fluctuations of current owing to short-circuiting, abrupt making and breaking of the current, caused by the settling of the charge during the melting-down stage. From this defect the bottom electrode furnaces are nearly free.

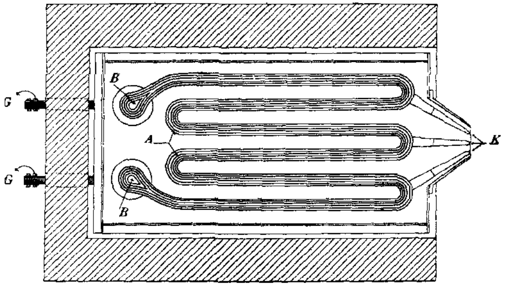


Fig. 26.—Gin electric furnace (Plan).

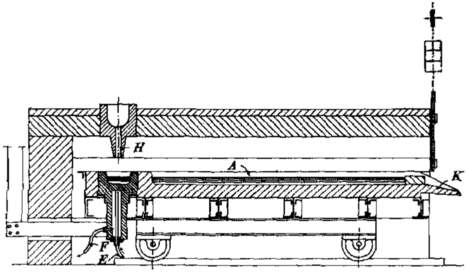


Fig. 27.—Gin electric furnace (Vertical section).

Gustave Gin has patented a resistance furnace for the production of steel which, though at present not worked on a large commercial scale, shows so much of interest that a description will not be out of place.

The charge is contained in a channel, A, in a refractory lining, and constitutes a resistance through which the current flows from the terminals B B (see Fig. 26). A vertical section is shown in Fig. 27. The terminals are water-cooled, the connection being shown at E F (Fig. 27). Fused pig is run in at H, and scrap or ore may be added: tapping takes place at K. The whole arrangement is similar to an open-hearth gas-fired furnace, except that the heating is electrical, and is applied direct to the charge, and boxed in by the roof, instead of being produced in the vault of the furnace, and reflected from the roof on to the charge.

Induction furnaces differ from all others in being destitute of electrodes. Briefly, they are transformers. The current supplied to the primary of many turns is converted into heat in the secondary, which has a single turn, and consists of the steel to be heated. The best known examples of this type are the Kjellin and the Roechling-Rodenhauser furnaces, the construction of which is shown in Figs. 28 and 29. The latter has, in addition to the induced current, a current passed through the metal from electrodes buried in the walls, and may, therefore, be regarded as a combination of an induction and resistance furnace. In the case of the Kjellin furnace (Fig. 28) the materials to be heated are placed in a chamber in the form of a ring, A A, contained in a furnace of refractory firebrick. In the centre of this ring-shaped furnace is one end of a rectangular armature of soft iron, C, the other parts of which surround the ring in such a manner as to form a link with it. A current of 3,000 volts and 90 amperes is used to excite the armature, and at each reversal a corresponding current of low potential (about 7 volts and 3,000 amperes) passes, by induction, through the materials in the ring. These, in consequence, become strongly heated, owing to their resistance, and it is possible to produce steel with any desired content of carbon by the use of steel scrap, iron ore, and the necessary addition of ferro-manganese or ferro-silicon. Since there is practically no elimination of impurities during the process, calculated proportions of high-class materials only can be used. The disadvantages of this type of furnace are that, in view of the narrow ring channel, it is difficult to maintain basic slags sufficiently hot and fluid to do the necessary work, and, further, that the power factor of these furnaces is always low. These disadvantages are said to have been largely overcome in the Roechling-Rodenhauser furnace, in which the molten mass is subjected to a double heating effect, one direct by induction, and the other from the currents passing between opposite sets of electrodes. In the illustration appended (Fig. 29)

the smelting troughs B are seen to run together to form a wide central hearth, A. The protecting walls which surround this central hearth are built up of magnesia, or dolomite, and conduct very well at high temperatures. Behind the protecting walls are pole plates connected to the secondary circuit of the transformer, and from these pole plates currents flow through the

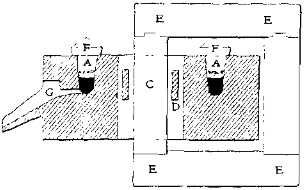


Fig. 28.—Kjellin induction furnace.

A, A, Circular trough in which steel is melted and treated; C, magnetic core; D, primary coil; E, frame connecting ends of C; F, cover for melting chamber; G, spout.

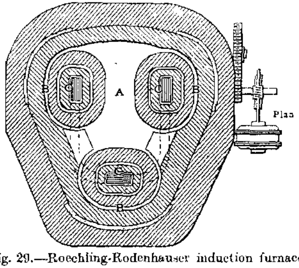


Fig. 29.—Roechling-Rodenhauser induction furnace.

A, Basin for molten steel; B, three narrow channels in which steel lies; C, three cores and coils for inducing current in the steel.

fused metal contained in the wide portion of the hearth. The latest form of this furnace, which is a tilting furnace of 15 tons capacity, is operated by three-phase current with a frequency of 50 periods. It is being used principally for refining Bessemer or open-hearth steel.

Various modifications of the Kjellin furnace have been recently introduced, but these involve no new principle. The essential feature of the Frick furnace, for instance, is the placing of the winding of the primary circuit above the secondary—*i.e.*, above the smelting hearth—while the Hiorth furnace is a double hearth induction furnace specially designed for continuous working. The Kjellin furnace has been in successful operation at Gysinge, Sweden, since 1900. A Frick furnace is in use at the Krupp Works, Essen. At the time of writing there are operating or in construction in this country three furnaces of the Kjellin type, two of the Frick type, and one Héroult furnace.

In regard to the chemical reactions which take place in the electric furnace, the complete removal of phosphorus is effected by the slightly oxidising slag combined with its high basicity and fluidity. The complete removal of sulphur is not so easily explained. The latter depends ultimately on the formation of calcium sulphide, and is facilitated by a reducing atmosphere. In an oxidising atmosphere calcium sulphate is liable to be formed, when the sulphur may pass back again into the metal according to the equation—

$$CaSO_4 + 4Fe = FeS + 3FeO + CaO.$$

The slag, also, should be highly basic and free from oxide of iron. According to Osann, the latter prevents desulphurisation, because of the exothermic reaction—

$$FeO + CaS = FeS + CaO.$$

Dr. Geilenkirchen explains the removal of sulphur in the Héroult furnace as due to the action of calcium carbide formed in the slag, which, by its reducing action, first deoxidises the metal and reduces the oxides in the slag, and then removes the sulphur according to the reaction—

$$2CaO + 2FeS + 2C = 2CaS + 2Fe + 2CO.$$

This explanation is inadequate for induction furnaces in which calcium carbide cannot be formed, although the removal of sulphur is equally effected. For the complete removal of sulphur the addition of some powerful reducing agent seems necessary. This, of course, is only possible after the removal of the phosphoric slag, as otherwise the phosphorus would be reduced and pass into the metal. Prof. Osann's investigations led to the adoption of ferro-silicon as the reducing agent, which is added after removal of the phosphorus. The use of ferro-silicon

has the advantage that its oxidation at the expense of the oxide of iron produces considerable heat, and raises the temperature of the hearth.

With regard to the energy required for the production of electric steel, it may be assumed that, starting with a cold charge, 800 to 1,000 kilowatt hours is required per ton of steel, while if molten metal is used only about 200 kilowatt hours, or even less, is required per ton. At present it appears that the true province of the electric furnace is not the manufacture of vast quantities of cheap material, but to supplement the work of the converter and open-hearth furnace, and to replace the crucible furnace in the production of smaller quantities of steel of the very highest grade, of special steel, and iron alloys.

The production of ferro-chrome, ferro-silicon, and of many other special alloys of iron by aid of the electric furnace has now become a widely extended and successful branch of electro-metallurgy. Of these manufactures, ferro-silicon and ferro-chrome are the most important. Ferro-silicon containing up to 10 or 15 per cent. silicon can be made in the blast furnace, but for the higher grades which are difficultly fusible the use of the electric furnace is essential. The blast furnace limit for ferro-chrome is about 40 per cent. chromium. Ferro-silicon is made by reducing a good hæmatite ore mixed with silica, with carbon in a smothered arc furnace, or by heating together scrap iron, silica, and carbon. Ferro-chrome is made by reducing chrome iron ore with carbon, just as in the production of pig iron, except that a much higher temperature is necessary. Ferro-titanium is produced by Rossi by heating mixtures of titanic ore, aluminium, and scrap iron in suitable proportions in an electric furnace. Several firms now specialise in low carbon ferro-alloys, but the details of the processes are kept secret. The Giffre furnace is reported to be particularly successful for this purpose.

Ferro-manganese is considered under manganese (*q.v.*). The following analyses represent modern ferro-alloys as made in the electric furnace (P. Girod, Faraday Society, June, 1910) :—

	Ferro-vanadium.			*Ferro-molybdenum.*
V,	50·00	35·00	Mo,	77·50
C,	3·20	1·00	C,	3·50
Si,	0·40	0·12	Si,	0·40
Al,	0·20	0·12	Mn,	0·40
Mn,	0·60	0·12	P,	0·04
S,	0·05	} 0·03	S,	0·03
P,	0·50		Fe,	18·13
Fe,	45·05	63·61		
	100·00	100·00		100·00

Ferro-tungsten.			*Ferro-chromium.*		
W,	83·000	73·000	Cr,	64·50	63·50
Fe,	15·500	19·000	Fe,	22·00	35·00
C,	0·600	3·500	C,	9·50	0·60
Si,	0·400	0·400	Si,	2·25	0·20
Mn,	0·200	3·500	Al,	0·80	0·10
Ca,	0·151	trace	Mn,	0·15	0·10
As,	0·100	0·100	Ca,	0·25	0·35
Sn,	0·050	0·100	S,	0·04	0·03
S,	0·040	0·050	P,	0·03	0·02
P,	0·015	0·030			
	100·056	99·680		99·52	99·90

Ferro-silicon.			*Silico-Calcium-Aluminium.*	
Si,	30·50	88·50	Si,	55·00
Fe,	68·00	9·30	Ca,	22·00
Mn,	0·35	0·15	Fe,	15·00
Al,	0·10	0·15	Al,	5·00
Ca,	0·30	1·20	C,	1·25
Mg,	0·10	0·30	Mg,	·35
C,	0·35	0·25	Mn,	·22
S,	0·02	0·15	S,	·07
P,	0·04	0·03	P,	·03
	99·76	100·03		98·92

For further information on the subject of the electro-metallurgy of iron and steel, the reader is referred to Mr. F. W. Harbord's paper, which we have already quoted, "Electric Smelting," *Journ. West of Scotland Iron and Steel Institute*, 1909.

Frequent papers also appear in the following journals :—*Journ. of the Iron and Steel Institute; Trans. of the Faraday Society; Trans. of the American Electrochemical Society; Mineral Industry.*

COPPER.

The following are the chief sources of copper :—

Native Copper.—Considerable masses of metallic copper occur native in the neighbourhood of Lake Superior. In other districts —*e.g.*, in Cornwall—it is found in veins distributed, in crystalline form, through granites and other rocks. Copper sand containing 60 to 80 per cent. of copper, the balance being quartz, is found in Chili, and is known as "copper barilla." It constitutes a minor source of copper.

Red Copper Ore.—Pure specimens of this mineral (*cuprite*) have the composition Cu_2O. It is found in Cornwall, but the quantity is small compared with that of the sulphide ores. Black oxide of copper (CuO) (*tenorite*) is also found in slight amount.

Carbonates of Copper, *containing various proportions of*

copper hydroxide and copper carbonate, are found as *malachite*, $CuCO_3 . Cu(OH)_2$, and *blue malachite* or *azurite*, $2CuCO_3 . Cu(OH)_2$. The most noteworthy deposits of these minerals are those at Burra-Burra in Australia.

Copper Pyrites (*Chalcopyrite*).—This is one of the most abundant of copper ores. Pure specimens have the composition $Cu_2S . Fe_2S_3$, but the ores which are worked contain a certain amount of gangue and generally an excess of sulphide of iron, and are frequently associated with arsenic. Indeed, iron pyrites containing copper (see *Manufacture of Vitriol*, Vol. II.), is worked for the copper which it contains.

A variety richer in cuprous sulphide than is ordinary copper pyrites, corresponding with the formula $3Cu_2S . Fe_2S_3$, is known as *peacock copper* from its variegated colours.

Copper Glance.—This ore corresponds with the formula Cu_2S (cuprous sulphide). It is found in Cornwall, and occurs in Siberia, Saxony, and elsewhere.

Grey Copper Ore (*Fahl-ore*) consists of copper sulphide associated with antimony sulphide, its composition being very various.

Cupriferous Schists, consisting of bituminous shale through which copper pyrites and copper glance are disseminated, occur at Mansfeld.

Copper Oxychloride (*Atacamite*), $CuCl_2 . 3Cu(OH)_2$, occurs in several copper districts, but most abundantly in Chili and Bolivia.

WINNING OF COPPER FROM ITS ORES.

A. **DRY PROCESSES.**—The following general principles may be said to control the dry processes for the extraction of copper :—The production of copper from its ores differs essentially from that of iron by reason of the fact that the chief ores worked contain copper as sulphide instead of as oxide, and that sulphur, instead of oxygen, is, therefore, the element to be removed. Seeing that sulphur, unlike oxygen, cannot be removed by reduction with carbon, the formation of CS_2 being endothermic, it must first be eliminated as SO_2 by an oxidising process, the copper being converted into oxide.

If pure copper sulphides were being worked, reduction of the oxide to metal by carbon could be effected at this stage,* just as iron ores are reduced in a blast furnace; but, owing to the fact that iron is a constant constituent, the roasted ore would contain

* Actually, pure copper sulphide is capable of "self-reduction" (p. 172), thus :—$Cu_2S + 2CuO = 4Cu + SO_2$, so that complete roasting and reduction with carbon is unnecessary; it is, nevertheless, practised in typical German processes—*e.g.*, that which is known as the Mansfeld process (*v.i.*).

oxides of iron; these would also be reduced, yielding a mass which would prove unmanageable, on account of the infusibility of the iron. It thus happens that in any process for smelting copper from an ore containing copper and iron, the iron must be eliminated before the copper can be obtained as metal. In order to effect this, advantage is taken of the greater stability of copper sulphide than that of iron sulphide in an oxidising atmosphere.

When a mixture of the sulphides of iron and copper is roasted, the greater part of the iron is converted into oxide, while the bulk of the copper remains as sulphide. Even should these reactions be incomplete, in the sense that a portion of the iron remains as sulphide, while a portion of the copper is converted into oxide, all the copper may be ultimately obtained as sulphide on account of the ease with which oxide of iron and sulphide of copper interact. When all the copper has been obtained as sulphide and all the iron as oxide, the latter can be removed by suitable fluxes.

Approximately pure sulphide of copper having been thus obtained, it is only necessary to replace a portion of its sulphur by oxygen, and to subsequently cause the oxide of copper to react with the residual sulphide, thus :—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Crude copper differs from most other crude metals, in respect of the fact that it can be economically refined by electrolysis (*v.i.*), as well as by ordinary dry methods.

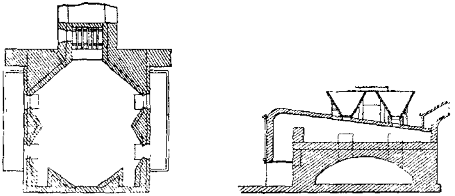
Although the processes for smelting copper are numerous and complicated, they all depend upon the general principles expounded in the foregoing paragraphs. The description of the **Welsh smelting method** will serve as one of a type to which others are referable. In this process the following operations are usually carried out :—

1. **Calcination.**—The object of this depends largely on the nature of the ore. In the case of copper pyrites, partial oxidation of the iron and sulphur and elimination of arsenic and antimony, are the chief ends to be attained.

It is unusual to attempt any method of preliminary concentration of copper ores, except when they are very poor (containing, say, 3 to 4 per cent. Cu). The loss in the process is always very considerable, and it is only in very few cases that mechanical concentration is profitable.

In the Welsh process calcination is generally effected in a reverberatory furnace, with a grate small in comparison with the hearth, so that the temperature is low enough for efficient calcination. A furnace of this type is shown in Fig. 30. The main reaction is the removal of about half the sulphur as SO_2, and the greater

part of the arsenic as As_4O_6. Antimony is also partly eliminated. The resulting fumes, "copper smoke," will contain, besides the above constituents, SO_2, evolved from ferrous sulphate, into which a portion of the iron sulphide has been oxidised, and HF from the interaction of the SO_3 with fluor spar (CaF_2) present in the gangue. These fumes are condensed as much as possible, and the arsenic recovered. The calcined ore consists essentially of copper as sulphide with some oxide; iron as oxide with some sulphide; a portion of the arsenic and antimony as arseniate and antimoniate; and unchanged gangue. Any zinc sulphide present is partially oxidised, while galena (PbS) is converted to a mixture of lead oxide and sulphate, and, if present in any quantity, interferes somewhat with the roasting on account of its fusibility. When the SO_2 is to be used for vitriol making,



Plan. *Elevation.*

Fig. 30.—Reverberatory roasting furnace.

calcination is performed in roasters, from which the fire gases are excluded (*e.g.*, muffles), and from which the SO_2 can be drawn off in a fairly concentrated form. Calcination can also be performed by roasting the ore in heaps, constructed essentially in the manner of a charcoal heap; a portion of the sulphur distils off and may be collected in hollows left in the heap. When poor ores are thus treated it is found that the centre of each lump has become richer in copper than its outer portion; a concentration is thus effected by this process, which is known as "kernel-roasting." The substitution of stalls (*cf. Coke Manufacture*, Vol. II.), for heaps is practised when the utilisation of SO_2 is required; the gas is drawn off through flues in the walls of the stalls. Narrow vertical kilns, with horizontal bars (*Gerstenhofer* kilns) down which the ore is caused to pass, meeting a current of hot air on its way, are also employed when calcination with the recovery of SO_2 is desired.

The Welsh process is seldom carried out now exactly according to the six stages we are attempting to describe, but it has been considerably modified from time to time, and among the improvements which have been introduced may be mentioned modern forms of roasting plant. Such furnaces are either intermittent or continuous. The tendency with reverberatory furnaces has been to increase their length to 20 or 30 feet, and to keep them narrow, while in America a series of furnaces is sometimes arranged end to end, the hearth of each being 2 or 3 inches higher than the ore before it. These multiple-hearth furnaces have a larger output, and are less costly for labour. Other intermittent furnaces possess rotating bodies, and are typified by the Bruckner calciner, which is really a reverberatory furnace consisting of an iron revolving cylinder lined with firebrick, about 8 feet in diameter and 15 to 20 feet long. At one end is a fireplace, and at the other end is a dust chamber connected with the flue and chimney. The cylinder rests on friction rollers, and is rotated by gearing placed on the exterior. Continuous roasting furnaces may be classified into—(*a*) *Tube furnaces*, consisting of revolving cylinders slightly inclined upwards from the fireplace, and similar in principle to the Oxland calciner employed for roasting tin ores (*q.v.*). (*b*) *Automatic reverberatory furnaces*, based on the same principle as the tube furnaces, and possessing very long hearths (120 feet upwards). The charge is turned over repeatedly, and slowly advanced along the furnace until it is discharged at the end by a series of rabbles or ploughs, which are drawn through the furnace by chains or otherwise. These furnaces may be either straight or curved (*e.g.*, the "horse-shoe" furnace). The O'Hara, Brown, and Pearce turret furnaces are examples of this class. (*c*) *Stack Furnaces.*—The old Gerstenhofer kiln already described is an example of this class. The Herreshoff furnace is based on a somewhat different principle. It is a circular stack furnace about 10 feet diameter and 10 feet high, consisting of a steel casing lined with firebrick. The ore travels from top to bottom over a series of shelves by means of ploughs attached to a central vertical shaft. About 5 tons of ore can be roasted in twenty-four hours. The ore used contains enough sulphur to supply the necessary heat once the action is started.

2. **Fusion for Coarse Metal.**—In this operation the bulk of the iron is to be removed as silicate. For this purpose it must all be present as a base (viz., as its oxide), and the residual iron sulphide, left by calcination, must, therefore, be converted into oxide. As has been already mentioned, this is to some extent effected by the interaction of the copper oxide, obtained in calcination, with the iron sulphide; but, as an auxiliary,

copper ores in which the copper is present as oxide are added.* The siliceous flux for the removal of the iron is provided partly by the gangue and partly by the slag from a succeeding operation, this slag, inasmuch as it contains about 4 per cent. of copper, being too valuable to throw away. The furnace in which the fusion for coarse metal is conducted is of the reverberatory type (see Fig. 31).

The hearth (from 30 to 40 feet long) is made of brick or of sand laid on bricks, and, since a high temperature is required, the ratio of fireplace to hearth area is comparatively large (about 1 : 14). The furnace shown in the diagram is provided with three telescopic steel double-charging hoppers for ore and one double hopper for coal. The firebox is provided with a blast pipe, and the ash is removed by cars running on rails. A depression in the hearth serves as a collecting well for the fused matte. The mixture of calcined sulphide ore and raw oxide ore (about 2 : 1) is introduced into the furnace through the hoppers, and the slag from a succeeding operation (thus worked up for its copper) is thrown in through the side doors. The furnace is then closed and the charge brought to fusion, in which condition it is maintained for six to seven hours. The slag is then raked out through the doors at the end and back into sand moulds.

The matte is drawn off through a tamping hole into ingot moulds. The slag, known as **ore furnace slag,** consists essentially of ferrous silicate, and should not contain much above 0·25 per cent. of copper; it is then regarded as "clean" and rejected. It is found difficult to obtain clean slags when working with raw material containing more than 15 per cent. of copper, and when the content falls below 9 per cent. the cost of heating the gangue becomes unduly great. The matte or "coarse metal" contains from 35 to 39 per cent. of copper, and has a similar composition to that of pure copper pyrites, the proportion of iron and sulphur having been reduced (see Table, p. 253).

3. **Calcination of Coarse Metal.**—The granulated or crushed matte is calcined in a reverberatory furnace with a large hearth. *The effect of this roasting is to substitute oxygen for a portion* of the sulphur, the main oxidation again taking effect on the iron sulphide, as in the original calcination of the sulphide ore. Calcination is sometimes carried out in a Gerstenhofer kiln, such as has been described on p. 241, so that SO_2 can be collected and used. The observations made as to modern methods of

* In the event of over-calcination, instead of under-calcination having taken place, the composition of the charge is corrected by the addition of sulphide ores instead of oxide ores.

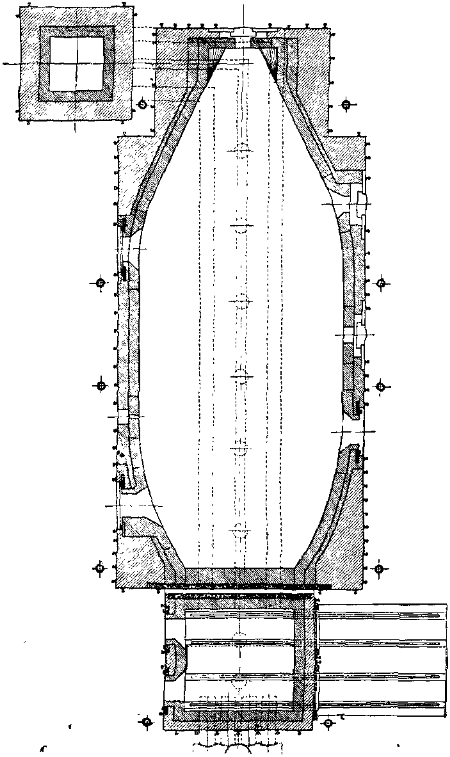


Fig. 31.—Reverberatory melting furnace (Plan).

roasting the ore in the first stage apply equally well to the calcination of the coarse metal.

4. **Fusion for Fine Metal.**—The calcined coarse metal is fused in a reverberatory furnace—which has a depression in the bed, and is in all respects similar to that used in the fusion for coarse metal—with oxidised ores and sometimes with crude copper precipitate from wet processes of extraction, and with rich slags from succeeding operations. The added oxidised ore may amount to as much as half the weight of the calcined coarse metal. The mixture is so proportioned that there shall be sufficient oxide of copper to react with the remaining ferrous sulphide,* and enough siliceous matter to flux the oxide of iron produced: the resulting matte consists essentially of cuprous sulphide, "white metal," containing about 70 per cent. Cu. Should the iron sulphide have been incompletely oxidised, "blue metal" containing 50 to 55 per cent. Cu is obtained, and in the event of the oxidation by means of the added ores having been pushed further than usual, self-reduction will occur and "pimple metal," containing about 76 per cent. Cu, will be produced. Pimple metal owes its name to its roughened surface, due to the escape of SO_2 from the metal as it solidifies. A portion of the copper is present in the metallic state, frequently having a fibrous mossy appearance (*moss copper*). The copper thus separated acts as a solvent for a large portion of such impurities as have persisted up to the present stage—*e.g.*, As and Sb—and settles to the bottom of the ingots into which the matte is cast; the upper and purer portions of the ingots are used for the "best selecting process" subsequently described, the lower portions going to the roaster (*v.i.*). The slags from the white metal consist of ferrous silicate, but inasmuch as the charge is rich in copper oxide, some copper silicate passes into the slag (**metal slag** containing about 4 per cent. of copper). To recover this copper the slag is returned to the furnace for fusion for coarse metal, already described.

For the production of a 70 per cent. regulus,† two fusions or smeltings are necessary, as we have described. Such a regulus is converted into "coarse metal" in a reverberatory furnace in the fifth stage, as described in the next section. In modern practice, however, it is customary to run for a 50 per cent. regulus

* A further adjustment of the proportion may be requisite if it has been disturbed by the introduction of crude copper precipitate, which may be provided with the necessary sulphur by the addition of sulphide ores.

† In America the old terms "coarse metal," "white metal," etc., are not used, but the regulus is always called a matte, and its richness is indicated by the percentage of Cu which it contains.

which is suitable for treatment in the "converter," the use of which is discussed later, and this may be done either in one stage or two, according to the richness of the ore. In the older Welsh process these smeltings were always carried out in reverberatory furnaces in the manner described above, and these are still used to a large extent, especially when the ores are in a fine state of division. In other cases some form of blast furnace is now generally used for smelting, their advantage being a larger output and economy in labour and fuel. There has been a considerable development in size and method of working smelting reverberatory furnaces, their capacity being increased from 12 to upwards of 50 tons per twenty-four hours. This increase in smelting capacity is not only due to increase in size of the furnaces, but to improvements in the method of working, such as rapid charging of the hot calcined ore, preheating the air by conducting it through channels in the brickwork, rapid skimming through four doors simultaneously, and tapping after several charges have been smelted, thus keeping the hearth well covered with matte. In America, recently, tilting furnaces have been introduced, similar to the Wellman furnace used in steel making (*q.v.*).

As we have indicated, blast-furnace smelting is now largely practised, especially for ores in the lump form, or for ores which have been converted into a porous mass by a process of "sintering roasting." The earlier furnaces were built of masonry, and were either circular or rectangular in section. The Orford furnace is of masonry, and is rectangular, being about 10 feet high, 12 feet long, and 3 feet 6 inches wide, and provided with 14 twyer openings arranged about 10 inches above the hearth. Modern improvements consist in the replacement of the brick furnaces by water-jacketed iron furnaces, which are more easily constructed, more durable, and simpler to manipulate. The larger sizes are nearly always rectangular. Some are entirely water-cooled, while others have only the lower portion or bosh water-jacketed, the upper portion being of masonry, and supported on columns as in the ordinary blast furnace used for iron ores. Suitable arrangements are made for tapping fused slag and matte. The furnaces are from 10 to 30 feet in height, and their smelting capacity commonly varies from 100 to 200 tons of ore per twenty-four hours with a consumption of 2½ to 3 cwts. of coke per ton of ore. To avoid the rapid destruction of the brickwork of the hearth by prolonged contact with the fused slag, it is customary to practise "outside separation" of matte and slag—*i.e.*, the liquid material is collected in a separate chamber or "forehearth," which is an iron vessel lined with firebrick and usually mounted on wheels, and from which the slag and matte are

tapped. The blast used in these furnaces rarely exceeds 1 lb. pressure, and the air is usually heated before entering the furnace.

Pyritic Smelting.—In ordinary matte smelting the heat is supplied by the combustion of the added fuel; the atmosphere is reducing, and nearly all the sulphur present enters the matte. By pyritic smelting is meant the smelting of sulphide ores by the heat generated by their own oxidation and without the aid of carbonaceous fuel. In this direction great progress has been made in recent years. In pyritic smelting, therefore, ores high in sulphur are used and an oxidising atmosphere is maintained. The furnaces most suitable are large rectangular water-jacketed blast furnaces with a larger number of twyers than usual, supplying a large quantity of hot air; furnaces with circular hearths are also used. In practice it is found advisable to add a small quantity of fuel (up to 5 per cent.) to the charge. The addition of a siliceous flux is also sometimes necessary. The process is particularly applicable to the concentration of mattes. One application of the method is to smelt together a mixture of pyrites low in copper and siliceous material carrying gold and silver, the object being to obtain a matte which contains practically the whole of the precious metals, and which is afterwards treated for their recovery.

5. **Roasting and Self-Reduction.**—In order that self-reduction may be brought about, it is necessary to roast a portion of the matte to oxide so that it may react upon the remaining cuprous sulphide and form metallic copper and SO_2, according to the equation given above. The ingots of fine metal are placed on the hearth of a reverberatory furnace—similar to that used in the preceding process, but provided with a greater number of air inlets—and slowly melted down, free access of air being allowed and the slag being frequently skimmed off. The molten mass soon begins to boil with the escape of SO_2. The air ways are closed, the slag skimmed off the surface, and the "blister copper" run iuto ingots. The escape of gas from the molten metal renders it vesicular aud blistered on the surface. It contains about 98 per cent. Cu. The slags (**roaster slags**) result from the combination of the oxides of copper and iron with the silica of the furnace bed, and contain about 10 per cent. of Cu. They are worked up in the fusion for fine metal.

It will be seen that the processes hitherto described consist of oxidations alternated with reactious between oxides and sulphides, a crude copper being thus obtained. In order to effect the separation of the products of the reactiou between sulphides and oxides, in the form of a matte, a fusion is necessary, any remaining oxides being removed as slag. According to the older

Welsh reverberatory furnace method, three pairs of these two types of process—roasting for oxidation and fusion for reaction—are necessary, the last pair (*v.s.* sub-section 5) being performed in the same furnace, and thus appearing as a single operation. In a more modern method of working, however, this last operation is actually carried out in two stages, two-thirds of the "white metal" charge being first calcined in a continuous tube roaster, then mixed with the remaining third part of uncalcined charge and the mixture heated in the reverberatory furnace and converted into coarse copper. When the fourth operation (fusion for fine metal) has failed to produce a matte sufficiently pure for the final roasting, another pair of operations must be carried out in order to bring the copper up to a grade suitable for refining. The product of this extra inserted pair of operations is known as "coarse" or "black copper," and contains about 80 per cent. of Cu. It is roasted to blister copper as already described.

An alternative method of carrying out this operation is to blow air through the molten mass in a converter. This process of "Bessemerising" copper matte is now in general use throughout the copper districts of America and in other parts of the world. A third method of obtaining copper from copper matte is to roast it to oxide and reduce with carbon as described below in the Mansfeldt process. This method is only used when silver has to be separated at this stage.

The Use of the Bessemer Converter in obtaining Coarse Copper.—The advantage gained by the use of the converter in refining iron chiefly consists in the circumstance that the impurities, in the process of removal by oxidation, themselves furnish the heat necessary to carry on the operation and keep the metal thoroughly liquid. In the case of iron, the chief impurities, carbon, silicon, and manganese, evolve much heat on oxidation, and thereby actually raise the temperature of the charge in spite of losses of heat by radiation and other causes. With copper, on the contrary, the chief impurities, sulphur, iron and arsenic, have comparatively low heats of combination with oxygen, and are also usually smaller in quantity than the impurities in iron. It follows that although the specific heat of copper (0·095) and its melting point (1,080° C. = 1,976° F.) are lower than the same constants for iron (0·112 and 1,505° C. = 2,741° F.), the heat evolved in bessemerising crude copper (*e.g.*, blister copper) is insufficient to maintain the metal in a molten condition. The attempt to refine crude copper by ordinary bessemerising has, therefore, been abandoned, and the old refining process (described in section 6), costly in fuel and labour, retained of necessity. By starting with a cruder product than blister copper, and thus

increasing the quantity of combustible material, it is possible, however, to evolve sufficient heat to maintain the charge in a liquid condition, and to oxidise it until the bulk of the sulphur

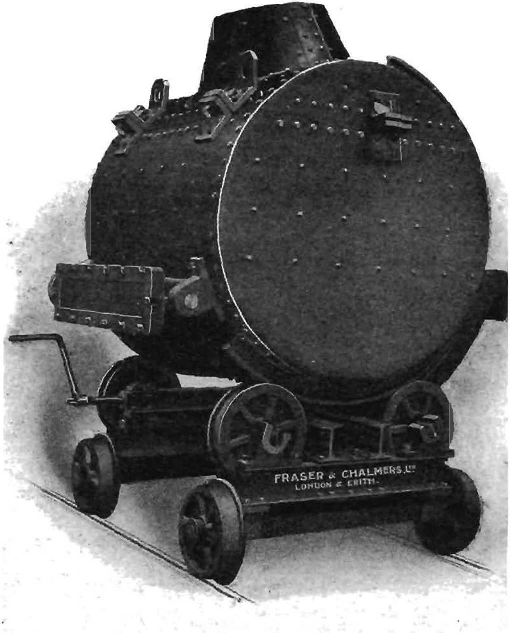


Fig. 32.—Bisbee copper converter. Capacity, 1½ tons.

and iron is eliminated and a grade of crude copper corresponding with the blister copper of the Welsh process obtained.

The **Manhès process** is based on this principle. A matte corresponding with blue metal—*i.e.*, of a composition between that of coarse metal and fine metal (*v.s.*)—is produced, run into a converter, and oxidised by a blast directed at first from below the charge and afterwards from twyers from the side of the converter, so that as the copper is reduced to metal and sinks to the bottom of the charge, it may cease to be acted on by the blast, which is directed upon the still unoxidised and specifically lighter matte.

The process can only be satisfactorily applied to mattes containing about 50 per cent. copper. If the matte is too high in copper the quantity of iron and sulphur is so small that the heat evolution is insufficient to keep the mass melted, while if the proportion of copper is too small the amount of slag produced is large and the destruction of the converter linings rapid. Modern copper converters usually take the form of horizontal cylinders mounted on friction wheels (Fig. 32), so that they can be easily tilted. The converter shell is made of ¼-inch steel plate lined with

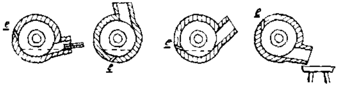


Fig. 33.—Converter—*e*, a twyer.

a layer (about 1 foot thick) of crushed quartz and a little clay. This lining furnishes the silica for "slagging" the iron oxide formed by the oxidising action of the blast, and usually lasts for about nine charges, after which the converter needs relining. This lining forms a somewhat expensive item in the process, and in some American Works it is the custom to use a siliceous ore containing from 5 to 10 per cent. copper as a lining, the copper being extracted during the process.

One form of converter consists of a cylindrical vessel with its longer axis horizontal and provided with an inlet and outlet at its ends, so that the flame of a furnace can be turned through it in order to melt the charge within it before bessemerising. As a rule, however, the converter is charged with molten matte. The twyers are placed in a row along the side of the cylinder, and are so connected with the pipe conveying the blast that by a partial rotation of the cylinder the air may be either forced through the molten charge at any desired depth, or directed down upon its surface without breaking joint with the air supply. A cross-section of the cylinder in different positions is shown in Fig. 33, *e* representing one of the twyers. The attachment

of a jointed tube capable of flexure to *c* for the conveyance of the blast will be readily appreciated. The process takes place in two stages, each lasting from 30 to 60 minutes. In the first or slagging period oxidation takes place, and the oxide of iron produced forms a slag of ferrous silicate with the lining of the converter. At this stage the slag is partially poured off. A little fresh matte is then usually added in order to supply fuel to bring up the temperature rapidly when the converter is again turned up. In the second or copper making period reaction takes place between copper oxide and sulphide with the production of metallic copper. The copper obtained has a composition averaging Cu 98·7, S 0·85, Fe 0·45 per cent.

6. **Refining.**—The crude blister copper usually contains S, As, Sb, Sn, Pb, Bi, Fe, Ni, Ag and Au. Of these, sulphur is the chief impurity, though copper from arsenical ores may retain several per cent. of arsenic. The refining process consists essentially of regulated and limited oxidation. The blister copper is piled on the hearth of the refinery, which is an ordinary roasting furnace with an inclined hearth, and slowly fused in an oxidising atmosphere. The charge is rabbled and skimmed at intervals until it has arrived at the stage of "dry copper," so called from the dull red colour of a fractured surface. This condition is due to the presence of cuprous oxide dissolved in the copper, and is an indication that the impurities have been oxidised. It is considered that the process of oxidation is much promoted by the conveyance of oxygen in the form of cuprous oxide to the interior of the mass of fused copper on the refinery hearth. A similar but more efficient agent is sometimes used—viz., oxide of lead (produced by the addition of metallic lead to the charge), which is more easily reducible by the impurities to be oxidised than is cuprous oxide; this method of treatment is termed "scorification." The slag (**refinery slag**) contains the above-mentioned impurities as oxides—except that some of the sulphur and arsenic has been volatilised—and silica from the furnace lining. It also contains much copper oxide (corresponding with a content of about 55 per cent. Cu in the slag), to recover which the slag is reworked in the fusion for fine metal.

Dry copper containing cuprous oxide is useless for most purposes, being brittle ("short"); accordingly, as soon as the slag is removed, the surface of the metal is covered with anthracite or charcoal, and after a short time a pole of green wood is worked in the charge. The gases thereby evolved from the wood effect the reduction of the cuprous oxide and toughen the metal, converting it into "tough-pitch copper." It is found advantageous not to push the *poling* too far, as a small quantity of cuprous

oxide improves the quality of ordinary copper (see *Influence of Impurities on Copper*, p. 262). The tough copper is ladled into ingots. The substitution of other reducing agents for the carbon of the poling has been attempted, the greatest success having attended the use of phosphorus, in the form of copper containing 7 per cent. of this element. Only traces of phosphorus remain in the finished copper. Aluminium and zinc will effect a similar reduction.

WELSH PROCESS OF COPPER SMELTING.

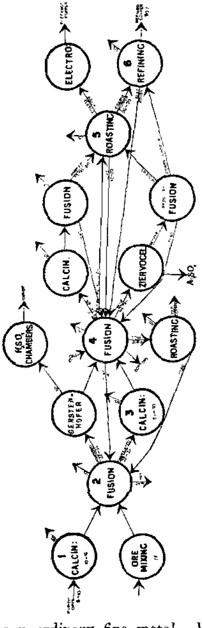


Fig. 34.

The removal of arsenic from arsenical blister copper and arsenical copper bottoms (*v.i.*) is advantageously effected by refining in a furnace with a basic-lined hearth, such as is used in steel-making, because impurities yielding acid oxides—*e.g.*, arsenic and antimony—are thus more easily eliminated.

Process of making "Best Selected" Copper.—It has already been indicated that when oxidation occurs, in the process of fusion for fine or white metal, beyond the point at which all the iron is converted into oxide, a portion of the copper *appears as metal, and this* dissolves a large proportion of the impurities of the matte. It is found advantageous to exaggerate this effect, and to thus obtain a matte which can be more efficiently refined than can ordinary fine metal. When this method is adopted, the process is conducted in a separate furnace, in which the fine metal, instead of being made to undergo complete self-reduction, as in the roaster furnace (*v.s.* sub-section 5), is melted

down, and is tapped when about one-fourth of the copper has been reduced. When the matte is cast into ingots, the metal settles to the bottom, and is afterwards broken off. The refined matte ("close regulus," containing 79 per cent. of Cu) is almost pure Cu_2S (which contains 80 per cent. of Cu), and is put through the roasting and refining process already described (Nos. 5 and 6). The copper thus obtained is "best selected." The lower portions of the ingots are known as "bottoms," and are rich in the impurities (notably arsenic) present in the original fine metal. They are refined in the same manner as is blister copper, preferably on a basic hearth, and yield a copper of a grade lower than best selected. The "B.S. process" is now seldom used. The so-called "best selected copper" of commerce is now usually prepared from pure materials.

The diagram on the preceding page (Fig. 34) gives a graphic representation of the stages of the Welsh process of copper smelting.

The gradual change in chemical composition of the products of copper smelting by the Welsh process, from the ore to tough pitch copper, is shown in the accompanying table of analyses :—

	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	Fine Metal.
Copper, .	12	13	34	37	72
Iron, . .	26	28	35	38	6
Sulphur, .	30	21	30	15	22
Gangue, .	32	34	1	1	...
Oxygen, .	...	4	...	9	...
	100	100	100	100	100

	Bottoms.*	Blister Copper.	Refined Copper.	Tough Pitch Copper.	Best Selected.
Copper, . .	92·32	98·46	98·90	99·61	99·89
Sulphur, . .	0·95	trace	trace	trace	...
Lead, . .	0·92	0·02	0·02	0·02	trace
Bismuth, . .	0·06	0·04	...	...	0·02
Arsenic, . .	5·09	0·84	0·02	0·02	0·05
Antimony, . .	0·27	trace	trace	trace	trace
Phosphorus, .	0·05	0·01	...	...	...
Iron, . . .	0·02	0·02	trace	trace	trace
Nickel and cobalt,	0·12	trace	0·22	0·21	trace
Silver, . .	0·02	0·02	0·03	0·03	...
Oxygen, . .	...	...	0·75	0·08	...
	99·82	99·41	99·94	99·97	99·96

* *Journ. Soc. Chem. Ind.*, 1891, p. 4.

The products obtained in copper smelting and refining necessarily vary according to the nature of the raw material and the mode of working: the figures given above are, therefore, to be taken as representative examples and not as rigid standards.

Typical German Process of Copper Smelting.—This differs from the Welsh process already dealt with, in that kilns and blast furnaces are respectively substituted for the calcination furnaces and fusion furnaces described above. Moreover, the fine metal is roasted "dead"—*i.e.*, converted into cupric oxide —and reduced by carbon in a reverberatory furnace, this pair of operations taking the place of the self-reduction of the Welsh process. For most ores the Welsh is now largely substituted for the German typical method, as although it needs more fuel it avoids the strong reducing action of the blast furnace which tends to yield an impure metal.

The Mansfeld Process of Winning Copper (and Silver).—This process is particularly adapted for ores poor in copper, but containing sufficient silver to pay for recovery. This is especially the case with the Mansfeld cupriferous schists. A typical ore of this class has the following composition:—

	Per cent.
SiO_2,	32·78
Al_2O_3,	11·28
CaO,	14·31
MgO,	4·53
CO_2,	13·51
Fe,	0·85
Cu,	2·93
Ag,	0·01
S,	3·96
Bituminous matter, &c.,	14·07
	98·23

The ore is burnt in heaps; the bitumen and some of the sulphur are eliminated, but care is taken to retain the copper as sulphide. It is then fused in blast furnaces with slags from a succeeding operation and fluor spar. The resulting coarse metal contains from 30 to 45 per cent. of copper, and was formerly roasted in kilns, for which purpose it was mixed with about its own weight of already roasted coarse metal to avoid fusion. In modern works the coarse metal is calcined in reverberatory furnaces exactly as in the Welsh process. The fusion for fine metal (*spurstein*) is conducted in a reverberatory furnace. As it is important that "moss copper" (*v.s.*) should not separate, some unroasted coarse metal is added to the charge to keep the copper as sulphide. The fine metal contains 74 to 75 per cent. of Cu and 0·3 per cent. of Ag. The next process has for its object

the complete oxidation of the copper, and, concomitantly, the *conversion of silver into sulphate. This is carried out (in Ziervogel's process)* by roasting the ground fine metal in a reverberatory furnace, and can only be effected by due attention to the conditions of oxidation: these will be dealt with *more* particularly under *Silver*. The silver sulphate is leached out, precipitated by copper and worked up. The residual copper oxide is dried, mixed with small coal, reduced in a reverberatory furnace, and refined in the usual way. The method described for the recovery of silver is now seldom used, the "spurstein" being run directly for coarse copper.

WET PROCESSES OF COPPER EXTRACTION.—When ores *containing copper sulphide are exposed to air in a moist condition*, the sulphide is oxidised to sulphate and may be leached out with water. The methods depending on the application of *this, and like principles, are available for ores containing about* 3 per cent. Cu, which are too poor to smelt profitably. In certain copper-bearing strata this extraction takes place naturally, yielding a solution of copper sulphate, the "blue-water" of some copper mines. The same process is put in use artificially by spreading the ore in heaps, provided with trenches to act as drains, and frequently watering it during many months. Owing to the slow oxidation of large masses of ore in this way, *a considerable quantity of heat is generated; the temperature* is best kept as 38° C. = 100° F. by regulating the water supply, for the production of steam would exclude air. On the other *hand, too low a temperature unduly retards the process*. The oxidation proceeds mainly at the expense of the copper sulphide, and when this is nearly exhausted (*e.g.*, to 0·25 per cent. Cu) the ore is still serviceable as a sulphur ore (for vitriol making). The solution of copper sulphate, whether obtained naturally or artificially, is run into asphalted tanks filled with iron pigs, by means of which the copper is precipitated; the crude product (containing 65 per cent. of Cu, the balance being chiefly graphite *and rust) is sent into the market as "cement copper."* The presence of much ferric sulphate (from the iron sulphide of the ore) in the liquors frequently causes the consumption of three *times as much iron as is necessary to precipitate the copper*, the difference being due to the reduction of ferric to ferrous sulphate. It is advantageous, as far as economy of pig or scrap iron is concerned, to roast the ore before extraction, as the amount of ferric sulphate in the liquor is thus decreased and the amount of pig iron consumed by it correspondingly diminished.

Large quantities of pyrites containing about 3 per cent. Cu are burnt for vitriol making, and the residue (chiefly ferric oxide)

worked up for copper. This is generally done by grinding the spent pyrites with common salt and calcining the mixture in a muffle furnace (the Henderson process). The sulphur left in the ore by the vitriol maker is oxidised, copper sulphate being formed. This reacts with the salt, yielding cupric chloride and sodium sulphate. The "chlorinated" ore is leached out with the liquors (containing HCl) that have been condensed in the towers attached to the furnace flues, and the copper is precipitated by iron in the usual way, any silver present being previously precipitated by means of sodium or zinc iodide. The silver is recovered by reducing the precipitated iodide with hydrochloric acid and granulated zinc and refining the metal thus formed. The spent ore, "purple ore," is used for the fettling of puddling furnaces. A similar chlorinating roasting is carried out in heaps at the mines when the sulphur is not utilised.

A simpler process for the separation of silver is by means of iron. The clear liquor is agitated by means of steam in a tank containing some thin sheet iron. A small portion of the copper together with all the silver and gold is precipitated by the iron. This copper precipitate is afterwards electrolytically refined and the precious metals recovered from the sludge, as described in a later section. Gibbs' process consists in passing a small quantity of sulphuretted hydrogen through the liquor when all the silver is precipitated with the first portions of the copper, the precipitate often assaying 200 ozs. per ton.

Another method of dissolving copper from its sulphide ores (the Doetsch process used at the Rio Tinto mines) depends on the fact that when a cupriferous pyrites is treated with a solution of a ferric salt—*e.g.*, Fe_2Cl_6—the cuprous sulphide reduces the ferric chloride with the formation of cuprous chloride and free sulphur,

$$Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S.$$

A portion of the cuprous chloride is oxidised by the air to cupric chloride. In practice, ferric chloride is not used, but a mixture of ferric sulphate and salt (potentially ferric chloride), such as results by adding salt to liquors from the precipitating tanks, or by leaching the chlorinated ore that has been roasted in heaps in the manner described in the preceding paragraph. The excess of salt serves to dissolve the cuprous chloride. The precipitation of the copper is effected as usual. The ferrous chloride is reconverted into ferric chloride by letting it fall down a tower up which a current of chlorine is passed, the latter being obtained by heating a mixture of salt, ferrous and ferric sulphates in a reverberatory furnace.

Oxidised copper ores, of course, do not need any preliminary

roasting, and are treated directly with any convenient acid liquor, the copper being precipitated from the solution by scrap iron in the usual way.

Another extraction process is that of Hunt and Douglas, which depends on the action of ferrous chloride on copper oxide. Sulphide ores must, therefore, be first roasted if they are to be treated by this process.

$$3CuO + 2FeCl_2 = Cu_2Cl_2 + CuCl_2 + Fe_2O_3.$$

If cuprous oxide is present metallic copper is precipitated.

$$3Cu_2O + 2FeCl_2 = 2Cu + 2Cu_2Cl_2 + Fe_2O_3.$$

The leaching agent is made from a mixture of ferrous sulphate and common salt, an excess of the latter being used to dissolve the cuprous chloride formed. The copper is precipitated from the solution by means of iron. The amount of salt and iron used is less than with the Henderson process. The objections of the process are the formation of basic salts, the difficulty of filtering the residue, and of recovering any silver present. These objections have led to a new Hunt and Douglas process, in which the ore is dissolved in sulphuric acid, and ferrous chloride or calcium chloride added to convert the copper into cupric chloride, sulphur dioxide being then forced through the liquor to precipitate cuprous chloride.

$$CuCl_2 + CuSO_4 + SO_2 + 2H_2O = Cu_2Cl_2 + 2H_2SO_4.$$

The cuprous chloride is separated and treated with iron to precipitate copper or with milk of lime to form cuprous oxide, which is afterwards smelted with carbon for the production of metallic copper. The solution from the cuprous chloride precipitate is freed from SO_2 by blowing in hot air, and is then available for dissolving a further quantity of ore.

THE ELECTROLYTIC WINNING AND REFINING OF COPPER.—As stated above, cement copper is a crude product containing 60 to 80 per cent. Cu, the remainder being impurities (graphite and rust) from the iron. By using electrical energy instead of the chemical energy of iron to reduce the copper, a pure metal can be obtained at a single operation; this is rendered possible because of the greater ease with which copper is deposited from an acid solution than is the chief impurity present —viz., iron—a fact which is borne out by the capability of iron to replace copper in its salts, as in the production of cement copper. An ideal process would be to win pure copper direct from the ore by using the ore as an anode (the electrode at which oxygen is evolved if the anode be non-oxidisable, or utilised

in oxidising and dissolving the anode, in the contrary case), and thus bringing the copper into solution, to be deposited again as metal, free from the other constituents of the ore, on the cathode. The difficulty of completely extracting the crude ore, by reason of the obstruction caused by the insoluble gangue and other constituents, renders this process impracticable. Even when the ore is first smelted to a matte (*e.g.*, coarse metal), and used as an anode, the same difficulty arises. At Mansfeldt, however, a process known as the Gunther-Francke process is now being worked with more or less success, in which anodes of 75 *per cent.* matte are used. The cathodes are thin copper plates, and the electrolyte is kept in constant circulation at a temperature of 70° C. Iron, nickel, and cobalt go into solution, and an "anode sludge" collects at the bottom of the vats. Sulphur is extracted from this mud by means of hot acetylene tetrachloride, and silver is recovered by means of sulphuric acid. At present two classes of process are chiefly employed in treating copper electrolytically, viz. :—(1) extraction of the ore as in a wet process, followed by the electrolysis of the cupriferous liquor; and (2) refining of crude copper of the grade of blister metal or black copper.

1. **Extraction and Electro-deposition.**—A typical process for winning copper from the ore electrolytically is that of Siemens and Halske. In this an ore containing copper as sulphide is first partially roasted to oxidise any sulphide of iron to ferric oxide, and then leached with an acid solution of ferric sulphate obtained at a later stage of the process;

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S.$$

Any copper oxide formed by roasting is also dissolved as sulphate. The liquor, containing copper sulphate and ferrous sulphate, is circulated first through the cathode compartments of a series of electrolytic tanks, and then through the anode compartments. In the former the copper is deposited on thin copper cathodes, and in the latter the ferrous sulphate, coming from the cathode compartments, is oxidised to ferric sulphate as it passes the anodes, which are of carbon. The solution of ferric sulphate is then used as described above for extracting the ore, the process thus being continuous. The cells are divided into anode and cathode compartments by porous diaphragms, which keep the liquor at the anode separate from that at the cathode, and prevent the ferrous sulphate being oxidised at the anode to ferric sulphate and reduced again at the cathode. In this way the liquor is returned to the leaching vats with its iron in the ferric condition. The cells are arranged one below the other, and a

constant flow of solution maintained. The difficulties experienced in obtaining suitable permanent anodes and diaphragms have led to several modifications of the Siemens-Halske process. In these the arrangement of electrodes and diaphragm has been horizontal instead of vertical, and the diaphragm has served not only as a separating membrane, but as a slow filter. Anodes of retort carbon or lead are used, while the cathodes may be copper sheets supported on wooden framework, or cylinders placed in the solution and kept in slow rotation.

In Hoepfner's process a solution of cupric chloride and sodium chloride is used in extracting the ore, by which means a solution of cuprous chloride in sodium chloride is obtained. Half of this passes to the cathode compartments, and half to the anode compartments. In the former copper is deposited, and in the latter cuprous chloride is converted into cupric chloride by the chlorine equivalent to the copper deposited upon the cathode. The cupric chloride solution is used to extract more ore, diluted with spent liquor (containing only sodium chloride) from the cathode compartment, again divided into two parts, and the cycle of operations repeated. The cuprous sulphide in the ore is extracted according to the equation—

$$Cu_2S + 2CuCl_2 = 2Cu_2Cl_2 + S.*$$

If, in leaching copper ores for an electrolytic process, the copper can be obtained in the cuprous state—that is, already on its way to reduction to metal—a sensible advantage accrues, as the current necessary for its complete reduction is correspondingly diminished. A subsidiary advantage claimed for the process is that cupric chloride is a solvent for silver contained in the ore; thus—

$$Ag_2S + 2CuCl_2 = Cu_2Cl_2 + 2AgCl + S.$$

The resulting silver chloride is fairly soluble in the solution of cuprous chloride in sodium chloride, and from the solution silver can be precipitated by well-known means—*e.g.*, treatment with metallic copper.

A process for obtaining copper from its ores electrolytically has been described by Keith. The ore is roasted and extracted with sulphuric acid. The solution is passed through a series of vats, in which it is electrolysed, and as the liquor is robbed of its copper on its passage, so is the current density decreased, not by diminishing the amperage of each vat, but by increasing the surface of the electrodes.

* This equation has been disputed, but has since been experimentally verified.

None of the above processes can be considered commercially successful, but are described as illustrating the principles on which processes of this kind are based.

2. **Electrolytic Refining.**—The refining of copper by electrolysis is a simpler matter than its winning by this means, and is more largely practised. The metal is obtained, by dry processes, as black or blister copper (containing 97 to 98 per cent. Cu), and cast into plates which are used as anodes in a bath of copper sulphate acid with sulphuric acid. In general it is not remunerative to refine very crude metal, owing to the rapid deterioration of the electrolyte. The latter usually contains 1½ lbs. copper sulphate crystals and ½ lb. sulphuric acid per gallon. The metal is dissolved by the action of the current, and deposited on the cathodes, which are thin sheets of pure copper. As the process consists solely in the transference of copper, and not in its true reduction, the only consumption of electrical energy is in overcoming the resistance of the bath. On this account a pressure of 0·1 to 0·2 volt suffices, although higher pressures varying from 0·3 to 0·6 volt are often used. A current density of about 10 amperes per square foot is generally used, as when the work is done at a higher rate, irregular deposition and spongy copper result. In some refineries, however, current densities up to 40 amperes per square foot are employed. Beyond this point special arrangements are necessary for circulating the electrolyte very rapidly. Electrolysis is usually carried out in the cold, but occasionally the electrolyte is kept warm, the temperature being sometimes as high as 50° C. Some of the impurities in the crude copper—*e.g.*, iron—go into solution as sulphates and gradually contaminate the electrolyte, until it has to be purified or renewed. Others—*e.g.*, gold, silver, and lead—remain as an insoluble sludge, from which the valuable constituents can be recovered. The composition of the sludge will evidently vary with that of the crude copper. An ordinary sample rich in silver will contain about 30 per cent. Cu (partly as oxide, antimoniate, sulphide, etc.), 30 per cent. Ag, and 30 per cent. $PbSO_4$, oxides of antimony and tin and the various small impurities, such as bismuth, sulphur, selenium, tellurium, and gold. A variation in working arrangements, at one time much practised in America (the Hayden process), consists in directly connecting only the end plates of a series with the dynamo used for yielding the current, and allowing the intermediate plates to hang free in the bath, one side of each acting as anode and the other as cathode, in regular order, according to the drop of voltage of the current from anode to cathode. This device saves numerous connections and allows of the complete immersion of the plates. The ultimate

effect is the conversion of each plate of crude metal, by continual deposition of pure metal on one side (functioning as cathode), and removal of crude metal from the other (functioning as anode), into a plate of pure metal. The irregularity of the action is the chief difficulty of the process.

Various methods have been devised for depositing copper in the form in which it is to be subsequently used. One of these is that devised by Elmore. In this process the cathode is a roller of metal, or wood coated with plumbago so as to be conductive. This roller revolves on bearings which also serve to convey the current to it. As the copper is deposited it is smoothed down and compressed by means of a heavy burnisher, which travels backwards and forwards over the surface of the roller. The copper tubes are afterwards stripped from the rollers, and are regular in shape and in structure. For the manufacture of wire a tube made in this way is cut spirally from end to end into a strip of square section capable of being drawn down into wire in the usual way. In the Cowper-Coles process copper is deposited in a smooth continuous sheet, so that it can be used at once without fusing or reworking. It consists in depositing the metal on a cathode rotating with a peripheral speed of 1,000 feet per minute in a hot solution of copper sulphate fairly concentrated and rapidly circulated. Under these conditions a current density (200 amperes per square foot) far greater than that ordinarily used can be employed.

The following is a typical analysis of electrolytic copper :—

Cu,	99·97
As,	nil
Sb,	trace
Pb,	trace
Bi,	trace
Fe,	0·01
Ni,	trace
O,	0·02
	100·00

For the recovery of silver and gold from the anode sludge, the latter is washed and dried, sifted from fragments of copper, and cupelled with lead in the usual way, the silver and gold being left and parted by boiling with sulphuric acid or by electrolysis. Direct treatment of the sludge with boiling sulphuric acid is also practicable, the silver being converted into silver sulphate and dissolved by dilution with hot water, the silver solution being decanted from the lead sulphate and the silver precipitated with copper. The lead sulphate containing the gold can be reduced

by fusion with charcoal to an ingot of auriferous lead, which can then be cupelled, leaving the gold fairly pure. In the *Moebius* process the mud is melted and cast into anodes, from which the copper is largely removed by passing a current of low voltage in an electrolyte of copper nitrate. The silver and gold in the residue are then separated electrolytically.

USES OF COPPER.—The utility of this metal largely depends on its malleability and ductility, and it is on account of these properties, as well as on account of its fairly high tenacity and resistance to corrosion, that copper is used for tubes, fire-boxes, wire, and cooking vessels. Its resistance to corrosion by chemical dyestuffs, and the ease with which it can be engraved, make it peculiarly adapted for use as rollers for calico printers. Its high electrical conductivity adapts it for the construction of electric leads. It finds an extensive use in making alloys (see below). Its specific gravity is 8·9 ; it melts at 1,084° C. = 1,983° F.

INFLUENCE OF IMPURITIES ON COPPER.—On account of the existence of two distinct methods of refining copper—viz., the dry way and the electrolytic process—copper commercially employed may be divided into two classes—(1) that which contains a small, but still perfectly perceptible, amount of impurity, and (2) that which is almost chemically pure. The most characteristic impurity of the former is oxygen, which is intentionally left in the metal by stopping the poling process before complete reduction has been effected. Seeing that pure electrolytic copper, though somewhat soft, has a high tensile strength (up to 20 tons per square inch), is very ductile, and altogether reliable as a material of construction, the presence of oxygen in pure copper is not necessary to improve it. On the other hand, copper prepared by the dry process, and free from oxygen, is deteriorated in these same properties by amounts of foreign matter that are of little moment when a suitable quantity of oxygen is also present. Hampe has examined the effect of the addition of known quantities of such foreign elements as are found in copper prepared in the dry way, to pure electrolytic copper, and has found that the tensile strength and ductility are not appreciably impaired by arsenic and antimony up to 1 per cent. According to Roberts-Austen, bismuth, even 0·1 per cent., causes the copper containing it to be of low tensile strength and brittle, while as little as 0·02 per cent. makes the metal distinctly red short.

It is generally conceded that sulphur, bismuth, lead, and possibly iron have an injurious effect upon the mechanical properties of commercial copper. The same appears true of antimony but not of arsenic. Nickel, which is constantly present

in commercial copper, seems to have a hardening influence, but is not otherwise objectionable. It may be taken that when any of these harmful impurities in its elementary state is present in copper, its effect is more serious than when sufficient oxygen is present to retain the said impurity as an oxide. For this reason an impure copper poled to tough pitch will contain more oxygen (needed to counteract the effect of the impurities) than an approximately pure copper of the same mechanical properties will contain. Where copper has to withstand heavy wear, as in locomotive fire-boxes, a pure soft metal is possibly less advantageous than one somewhat harder from the presence of such impurities as arsenic and nickel.

For use as an electrical conductor, on the other hand, electrolytic copper is employed, as its conductivity is equal to, or exceeds, Matthiessen's standard taken as 100,* whereas copper made by dry processes has a conductivity ranging from 90 down to 50, on the same scale. The greatest effect in lowering the conductivity is that due to arsenic, 0·1 per cent. of which may lower it to 50; tin is similarly deleterious. Aluminium, although it should never be present, affects the conductivity almost as much as arsenic. Phosphorus also greatly reduces the conductivity, and has been added to allow the copper to be readily cast.

COPPER ALLOYS.—Considerable confusion exists in the classification of copper alloys, the terms brass and bronze being used indiscriminately by many manufacturers. They are best considered perhaps under three heads:—

(1) Brasses, consisting mainly of copper and zinc.
(2) Bronzes, consisting mainly of copper and tin.
(3) Miscellaneous alloys.

(1) **Brasses.**—Alloys of copper and zinc, ranging from 88 per cent. Cu and 12 per cent. Zn to 50 per cent. Cu and 50 per cent. Zn, may be classed as brass: alloys of industrial value may be said to lie within the limits of 55 to 73 per cent. Cu. The available evidence points to the existence of a definite compound of copper and zinc represented by the formula $CuZn_2$, whilst two other compounds possibly exist having the formulæ CuZn and $CuZn_4$. Brasses may be classified as (*a*) **high brasses** containing more than 64 per cent. Cu. These alloys possess a simple structure, consisting of a single homogeneous solid solution, and can be rolled cold. The best class contains 70 per cent. Cu and 30 per cent. Zn; (*b*) **low brasses** containing from 55 to 64 per cent. Cu. These alloys are composed of two constituents, each of which

* Based on the conductivity of the purest silver available at the time of the preparation of the standard.

is a solid solution, and are suitable for hot rolling. The commonest alloy of this class is known as *Muntz metal*, and contains 60 per cent. Cu and 40 per cent. Zn. The above is, of course, only a general classification, there being no sharp limit between the two classes. (*c*) **Cast brass** varies considerably in composition and is usually very impure. It generally contains approximately 66 per cent. Cu and 34 per cent. Zn, and is known as *English standard brass*. It casts well, and is capable of being hammered and rolled. Brass is generally made by direct fusion of the metals in crucibles, for which a reverberatory furnace may be substituted when large quantities are required; in the latter case, however, the loss of zinc by volatilisation is very high. The ingots of copper are made red hot, then melted in crucibles, usually under a layer of charcoal to prevent oxidation, and the zinc then added. It is advantageous to first melt some scrap brass in the crucible, together with a little fluor spar or other flux, the copper being then added. A slight surplus of zinc is needed, both to combine with any oxygen in the copper and to compensate for loss by volatilisation. Lead, tin, and iron are sometimes intentionally added to brass for specific purposes, whilst arsenic, antimony, and bismuth are sometimes unintentionally present. Lead does not alloy with brass, but separates out in the form of films between the crystals of the brass, and thus tends to weaken the metal. High grade brass should not contain more than 0·30 per cent. Pb, or its ductility is impaired. The addition of 1 to 2 per cent. of lead is sometimes practised in making brass castings, which have afterwards to be turned. In this case tin should not be present, as it imparts hardness and strength. Tin is sometimes added to brass to render it less liable to corrosion by sea water when in contact with gun-metal. Such "*naval brasses*" contain approximately 62 per cent. Cu, 37 per cent. Zn, and 1 per cent. Sn. If more than 1 per cent. of tin is added the alloy becomes unduly hard and brittle. Iron is occasionally added to brass to impart hardness and strength. "*Aich's metal*" contains 60 per cent. Cu, 38 per cent. Zn, and 1·5 to 2 per cent. Fe. "*Delta metal*" is a ferruginous brass containing 55 per cent. Cu, 43 per cent. Zn, 1 per cent. Fe, and traces of lead and phosphorus. It is harder, stronger, and tougher than brass, and has a greater resistance to corrosion. "*Bull metal*," and the German "*Durana metal*," are similar alloys.

(2) **Bronzes** are copper-tin alloys varying from the material used in this country for bronze coinage (Cu 95 per cent., Sn 4 per cent., Zn 1 per cent.) to alloys containing as much as 25 per cent. Sn. The definite copper-tin compounds present in bronzes have been found to have the formulæ Cu_3Sn and Cu_4Sn. "*Gun-metal*"

usually contains from 8 to 14 per cent. Sn, and consists of a solid solution of tin in copper containing a certain amount of the definite compound Cu_4Sn. Gun-metal used for the manufacture of ordnance had originally the composition 91 per cent. Cu and 9 per cent. Sn, but since guns are no longer made of bronze the composition of industrial gun-metal exhibits considerable variation; thus, 87·5 per cent. Cu to 12·5 per cent. Sn is a common proportion. "*Bell metal*" contains from 15 to 25 per cent. tin and the remainder copper, large bells containing the largest amounts of tin. When strength and elasticity are required bronze should be as free as possible from lead, zinc, and iron. Lead, however, is sometimes added to bronze to enable it to be more easily turned or filed. The effect of lead on bronze is the same as on brass (*q.v.*). Zinc in small quantities has a very beneficial effect on bronze, combining with any oxygen present and giving good castings. Alloys with 16 to 18 per cent. Sn, 80 per cent. Cu, and 2 to 4 per cent. Zn and Pb are generally used for strong castings and bearings. Iron is sometimes added to bronze to impart hardness and tenacity. The effect of heat on some of the copper-tin alloys is remarkable, for whilst steel is hardened by quenching in water these alloys are hardened by slow cooling, and when quenched they lose their brittleness and become malleable.

Phosphor-bronzes, properly so-called, contain from traces up to 2 per cent. phosphorus, those most commonly employed containing from 0·5 to 1·5 per cent. and 8 to 12 per cent. tin. Their hardness varies with the amount of phosphorus, and is due to the presence of very hard particles of free phosphide of copper embedded in a softer matrix. They are well suited for the wearing parts of machinery. Phosphor-bronzes containing lead are used for bearing metals, an example of which is Dudley's "standard" phosphor-bronze containing Cu 79·6, Sn 10, Pb 9·6, P 0·8 per cent. Such an alloy consists of a sponge or skeleton of gun-metal having its interstices filled with lead. The term phosphor-bronze is also often applied to those alloys which are practically free from phosphorus, but in the manufacture of which this element has been used in an amount only just sufficient to act as a deoxidiser. The superiority of such alloys over ordinary bronzes is quite marked, and is due to the removal of dissolved oxides (as slag), in consequence of which they are more fluid and give castings free from pinholes. The absence of dissolved oxides also renders these alloys more resistant to corrosion. Phosphorus is usually added to bronze in the form of phosphor-copper or phosphor-tin, both of which contain from 10 to 15 per cent. P. The former is, in fact, a definite phosphide of copper, Cu_3P.

(3) **Miscellaneous Alloys.**—The so-called *manganese bronzes* are not really bronzes, as they seldom contain tin as an essential constituent. With 4 to 6 per cent. Mn these alloys retain their strength at high temperatures, and are used as fire-box stays. *The majority of commercial "manganese bronzes" contain* copper and zinc as their principal constituents, and are really brasses. *They invariably contain iron in addition to the manganese.* On account of their resistance to corrosion by sea water, manganese bronzes are used for ships' propellers. Much "manganese bronze" is free from manganese, this element having disappeared as slag after having served its purpose as a deoxidiser, leaving behind, however, the iron with which it was associated. Manganese bronzes to which aluminium has been added have recently been introduced under the name of "*Immadium*" alloys. They are very strong and tough, and remarkably resistant to the action of corrosive liquids. "*Aluminium bronze*" is likewise free from tin. The term is applied to alloys of copper and aluminium containing from 2 to 10 per cent. of the latter. They contain a definite compound $CuAl_2$, while a compound Cu_3Al *also exists. Small percentages of nickel or silicon are* sometimes added. These alloys can be employed for many purposes in place of brass, being readily forged and rolled, and drawn cold. "*Aluminium brass*" is ordinary brass containing less than 4 per cent. aluminium.

"*Cupro-silicon*" containing 30 per cent. silicon and "*cupro-magnesium*" are used as deoxidisers in the manufacture of copper alloys.

(See also p. 22; for copper-nickel alloys see under "Nickel.")

LEAD.

It is *doubtful* whether lead ever occurs *native*. The following are the chief ores of the metal :—

Galena (lead sulphide, PbS).—This is the most abundant and almost the only important ore of lead. Pure specimens of this mineral consist of cubical crystals which have a metallic lustre and a specific gravity of 7·5. Galena may be associated with silver sulphide without undergoing change of form. The presence of a very small quantity of silver—*e.g.*, 0·1 to 0·2 per cent. —constitutes the ore an argentiferous galena, but, as will be seen later, even smaller percentages may be remuneratively extracted. Galena frequently also contains gold.

Antimony is a common impurity of the mineral. The gangue in which galena is found is usually quartz, calcite, fluor spar or

heavy spar. Ores of copper and zinc often accompany galena. The principal lead mines of this country are those of Alston Moor, in the North of England, and of Derbyshire. The Scotch and Welsh mines are also of importance. The largest supply of lead is, however, obtained from America, both from the United States and Canada. The German deposits in the Harz and those of Spain and Australia are also considerable. Lead is, indeed, widely distributed throughout the world.

Cerussite (lead carbonate, $PbCO_3$) is extensively worked at Leadville, Colorado, where it is associated with galena. It occurs both amorphous and crystalline, and in the latter condition is sometimes black from the presence of lead sulphide.

Anglesite (lead sulphate, $PbSO_4$).—Originally found in Anglesea, whence its name. It is not abundant, though deposits occur in this country, Australia, and Peru. The mineral is often rich in silver, containing 30 to 100 ozs. of silver to the ton.

Many other lead compounds, such as the double chloride and carbonate, $PbCl_2 . PbCO_3$ (*phosgenite*), the chromate (*crocoite*), and the double chloride and phosphate (*pyromorphite*) are also found, but their comparatively small quantity renders them of little industrial importance.

It is usually found that the oxidised ores of lead—*e.g.*, lead oxide, carbonate, and sulphate—occur in the superficial lodes lying above those carrying galena. The same is true of zinc and copper ores, the cause of the phenomenon being the weathering of the original sulphides.

Preparation of Lead Ores for Smelting.—The substances constituting the gangue of the galena must be removed as far as possible before the ore is smelted, both because they occasion a loss of lead as fume and slag (dealt with in the description of the smelting of the ore—*v.i.*), and because the metals contained in them find their way into the finished lead. The main fact on which the concentration of lead ores is based, is that the galena has a higher specific gravity than the gangue. The ease with which the various constituents are separated depends, *pari passu*, on the difference of their specific gravity (galena 7·5, heavy spar 4·5, copper pyrites 4·3, blende 4·1, quartz 2·6). Mechanical separation resting on difference of specific gravity can only be applied when the gangue is intermixed with, but not disseminated through the galena, as the latter condition would necessitate reduction to a very fine state of division. The process of concentration is carried out by roughly crushing the ore and washing in a stream of water, the specifically lighter gangue being thus removed. When, however, argentiferous galena, containing its silver distributed through the gangue

instead of being in combination with the galena, is worked, concentration may cause serious loss of the more costly metal. Magnetic separators for removing iron pyrites have come into use in recent years. Oxidised ores are usually smelted without preliminary treatment.

The methods in use for smelting galena may be divided according to the reactions on which they depend.

1. **Partial Roasting and Self-Reduction.**—This is similar to that already described under copper (*q.v.*). When lead sulphide is roasted, it is partly converted into oxide with elimination of SO_2, and is partly directly oxidised into lead sulphate. Both oxide and sulphate are capable of reacting with lead sulphide (left when the roasting is incomplete) in the following manner :—

$$PbS + PbSO_4 = 2Pb + 2SO_2.$$
$$PbS + 2PbO = 3Pb + SO_2.$$

These are the main reactions, but other chemical changes may take place varying with the prevailing conditions. In presence of an excess of sulphur dioxide lead may be reconverted partially into sulphide and sulphate,

$$2Pb + 2SO_2 = PbS + PbSO_4.$$

2. **Complete Roasting and Reduction by Carbon.**—This process consists in roasting galena until the bulk of the lead is converted into oxide, though some passes into sulphate, and reducing it in cupolas or blast furnaces with carbon. The complete reduction of lead silicates that may be formed by the action of the lead oxide upon the siliceous gangue, is aided by the presence of iron ores naturally associated with the lead ores which are smelted in this manner. The action of the iron ore is probably due to the tendency of oxide of iron to form silicates, and thus, in the presence of carbon, to liberate lead from its silicates.

3. **Reduction by Iron** ("*Precipitation Process*").—In this process the sulphur of the galena is removed as iron sulphide, the lead being directly obtained in the metallic state.

The various methods thus catalogued may be dealt with as follows :—

1. **Self-Reduction.**—The first of the above methods is that generally employed in this country, and is typified by the Flintshire process. This is always conducted in a reverberatory furnace, shown in Fig. 35. It differs from ordinary furnaces of this kind in that the hearth is made from slag produced during the smelting, shaped into a depression or well, B, in the centre. The shaping is performed while the slag is hot and plastic, and the form is retained during the succeeding operation. The flame

from the hearth of the furnace, F, passes over the fire-bridge, and is deflected on to the charge, which is introduced through the hopper, T, and is worked through the side doors, o.

About a ton of ore is charged into the hot furnace and immediately spread over the hearth and stirred, while the air supply is carefully regulated until the charge has become pasty. During this part of the process the oxidation of a portion of the galena to lead oxide and sulphate takes place. Air is then excluded from the furnace, and the temperature is maintained at redness in order that the reaction of the sulphide with the oxide and sulphate respectively may proceed. The charge runs down into the well, where the lead collects at the bottom. The undecomposed ore and slag are chilled by opening the furnace doors, and, when semi-solid, pushed back on to the higher part of the hearth near the fire-bridge. The temperature is again

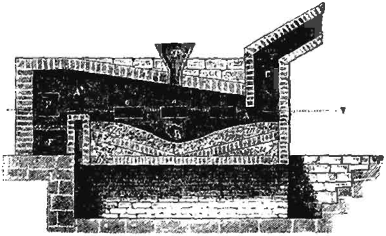


Fig. 35.—Furnace for smelting galena.

F, Hearth; T, hopper; o, side doors; P, stoking door.

raised until the charge runs down a second time, a fresh quantity of lead being reduced. The slag must now be rendered less fusible—*i.e.*, it must be "dried up" by throwing lime into the furnace. It is then sufficiently pasty to be again pushed back on to the higher part of the hearth, where it may now be again calcined. A third fusion follows, and should over-oxidation have occurred, a little coal is added to the charge as a corrective. The charge is now ready for withdrawal, save that there is lead disseminated through the slag. To recover this, another portion of lime is thrown in, and the pasty product pushed back on to the upper part of the hearth to drain. The crude lead is now run from the well into a tapping pot. Much dross collects on

the surface of the molten metal in the pot, and before removing this, the entrapped lead must be shaken out of it by agitation with a paddle and the introduction of small coal, the gases from which are ignited, the heat thus generated melting the metal in the dross. The lead is then ladled into pigs. Working with an ore containing 75 to 80 per cent. of lead a yield of 65 to 70 per cent. of lead is obtained, the balance being recovered by working up the slag and fume.

The first portion of lead obtained is purer than that subsequently reduced, and is sometimes tapped separately. The purity of the lead depends largely on the nature of the other metallic sulphides associated with the galena, which, in general, undergo reactions similar to those of lead sulphide itself. Silver and gold pass into the lead, while arsenic, antimony, zinc, etc., are partially reduced, and appear in the lead, and partially become associated with the slag, the remainder being volatilised. Antimony sulphide is a very objectionable impurity in the ore; firstly, because antimony makes lead hard, and secondly, because the oxide and sulphide being very volatile carry away both silver and lead in the fume. A good deal of lead oxide is volatilised during the above operations, and this, together with other volatile impurities, such as zinc, arsenic, and antimony oxide, constitutes flue-dust.* The quantity of such dust is greater the greater the quantity of volatile impurities, which carry over less volatile constituents of the charge. Lead fume is condensed by using very long flues (sometimes more than a mile in length). More complete condensation is effected by arrangements for lowering the velocity of the exit gases by first passing them through large chambers, and also by increasing the condensing surface either by means of baffle plates (Freudenberg plates) or by breaking up the main flue at intervals into a large number of smaller flues (Cowper flues). The flue length can be diminished by the use of various condensers, in which the fume is either pumped through water or submitted to the action of a water spray. Filtration through woollen or cotton bags has been found effective, and in some cases the product is suitable for use as a white paint. Attempts at electric condensation have so far not proved generally successful; the most promising is the *Cottrell process*, in which the current is passed through the flue gases from a high potential direct current machine between triangular wire frames covered with asbestos (attached to the + pole) and sheet iron (attached to the − pole). Condensed acid vapours and particles of dust are

* Hannay has asserted that the production of fume is dependent on the formation of compounds of SO_2 with PbS, stable at a high temperature, but dissociated on cooling. Evidence in this direction is still inconclusive.

deposited on the sheet iron, trickle down, and are collected at the bottom of the flues. The fume contains 60 to 80 per cent. of lead sulphate, small quantities of lead sulphide, lime, and zinc oxide.

The condensed fume is worked up with another charge. It is poorer in silver than is the original ore.

Modifications of the Flintshire process have been used in different parts of the world. In the Silesian furnace a low temperature is used whereby volatilisation losses are reduced, and a slag rich in lead (50 per cent.) is produced, which is afterwards smelted in the blast furnace. The celebrated Silesian process, however, has now been largely replaced by the Huntington-Heberlein process (*q.v.*) followed by blast-furnace work. The Flowing Furnace process once used in Cornwall was carried out in two stages: the ore was first calcined in a small reverberatory

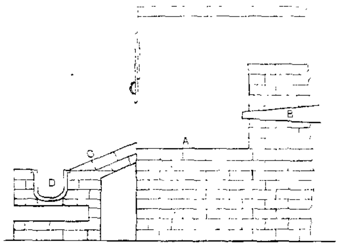


Fig. 36.—Scotch or ore hearth for smelting lead ores.
A, Iron box; B, twyer; C, work-stone; D, melting pot.

furnace and then smelted in a second furnace, a small proportion of scrap iron being added to aid reduction. The slag was tapped in the molten state and termed "run slag," while a liquid regulus of iron sulphide containing copper was also obtained.

It is in some places customary to carry out the self-reduction process on a hearth supplied with an air blast, known as the Scotch or ore hearth. This is a rectangular cast-iron box, A (Fig. 36), with a twyer, B, entering at the back. At the front of the box an inclined iron plate (the "work-stone"), C, slopes away from the furnace to the melting pot, D, which is kept hot by a separate fire. The furnace is first filled with coal, which is kindled. The ore is thrown on and partially roasted by means

of the blast. From time to time much of the charge is drawn on *to the work-stone, where the glassy "grey slag," rich in silicate* of lead, is separated from the unreduced ore and unburnt fuel, and put aside for treatment on the slag hearths (*v.i.*). During this selection the lead already reduced runs down a channel provided for it on the work-stone, and into the melting pot. The clinkered mass of fuel and ore, *browse*, is returned, fresh ore and fuel added, and the process continued. It is obvious that in this process the reducing action of the fuel plays a part, as distinct from the self-reduction of the ore. The process, moreover, differs from the reverberatory process in that oxidation and reduction are simultaneous, the oxide and sulphate reacting with the sulphide as soon as they are formed. Modern hearth furnaces are water-jacketed, use hot blast, and produce large quantities of lead fume. The process is of value in places where labour is cheap and fuel dear. The *Moffet hearth* furnace, one of the most modern, is shown in the accompanying diagram. It consists of two hearths separated by a hollow partition, in the lower part of which water is circulated. The wind-chest for the blast (not shown) is connected with the upper part of the partition, from which twyers descend and deliver the blast at the top of the hearth-box. The lead overflows from the hearth, and is delivered through a spout in the work-plate into the lead-kettle.

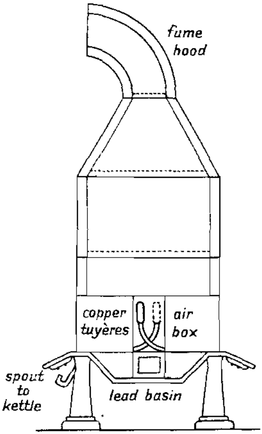


Fig. 37.—Moffet double-hearth furnace for lead.

The slags from both the Flintshire and the Scotch process are now usually treated either in a flowing furnace or a cupola. The slag hearth once universally used for this purpose still survives. The general object is to reduce the lead from the lead

silicate. For this purpose the slags are heated on a hearth with the aid of a blast, the proportion of acid to basic oxides being so adjusted as to yield a fusible slag irrespective of the decomposition of the lead silicate. The lead oxide is thus free to be reduced, and the lead is allowed to trickle away through a filter bed of cinders into the lead pot. The product, *slag lead*, is hard, *impure, and of low grade.*

2 and 3. **Reduction by Carbon and Iron in Blast Furnaces.**—One of the features in the progress of metallurgy has been the replacement of the reverberatory furnace by the more economical blast furnace. This, as we have seen, is the case in the metallurgy of copper, and is now to a large extent also true in lead smelting. The blast furnace method, which is most generally adopted, is found to be suitable for almost any class of ore, and the percentage of lead may be much smaller than that necessary for other methods, while the presence of silica to a certain extent is not disadvantageous. If the ore is free from sulphur (or has been roasted nearly free from sulphur) the case is analogous to the reduction of iron in the blast furnace, and it is only necessary to add some flux to form a slag with the gangue and fuel ash. Such a case of reduction by carbon pure and simple rarely arises, and it is unnecessary to consider it separately. *The flux may consist of iron ore and limestone, in which case* metallic lead and slag rich in ferrous silicate are produced. It appears that the ferruginous matter is reduced to the ferrous state and forms ferrous silicate with the silica of the lead silicate, the lead being simultaneously reduced to the metallic state by the carbon of the fuel, the presence of which determines the replacement of lead oxide, in its silicate, by ferrous oxide.

If, as is usually the case, the ore contains a large amount of sulphur, it is found best to remove a considerable portion of this by *roasting*; *otherwise the amount of iron consumed and of* regulus formed is inconveniently large. The so-called "*precipitation process*" in its simplest form consists in charging a reverberatory or blast furnace with galena and scrap iron (together with fuel in the case of the blast furnace), and raising the temperature until the following reaction sets in :—

$$PbS + Fe = FeS + Pb.$$

The products are metallic lead, a matte consisting of sulphides of iron, lead, and any copper and silver that may be present, and a slag consisting chiefly of silicates of iron. The matte is roasted and returned with the next charge, the operation being repeated until the copper content is 15 to 20 per cent., when the matte is worked up as coarse metal (see *Copper*, p. 243). It is economical

to substitute iron ore, burnt pyrites, or iron silicates from copper smelting (*q.v.*) *for metallic iron. The carbon of the fuel reduces* these substances, and the metallic iron thus produced removes the sulphur from the lead sulphide. This method, however, is seldom carried out as described; the most general method of lead smelting now consists in first roasting the ores to get rid of sulphur, and then smelting the roasted ore with fluxes and reducing agents in the blast furnace. The roasting is effected in heaps, shaft furnaces, or reverberatory furnaces, and the latter may be hand-worked or mechanically worked, while the Bruckner and other calciners are also used, exactly as described under copper (p. 242). "Sinter roasting" is also practised. In this method the charge is heated to such an extent that it agglomerates into a solid mass, which may be broken up into pieces of a convenient size for blast-furnace treatment. For this purpose the charge is made to travel along the bed of a reverberatory furnace until it is finally "sintered" in a specially hollowed out sump near the fireplace. For difficultly fusible ores "Colorado" roasters are used. These are simply stepped furnaces with three or four hearths, the last being, in fact, a reverberatory furnace arranged for fusion. The Dwight and Lloyd machine is largely used for continuous sintering of the ore in a thin layer. The damped material is delivered on to the face of a rotating drum formed of grate bars, and is immediately carried over some form of igniter. Air is then drawn through the ignited mass to maintain vigorous combustion, and the sintered material is afterwards removed from the drum automatically. Several new methods of roasting galena have been introduced, in which the ore is mixed with lime or gypsum, damped, and fed on to a small fire in a converter shaped vessel through which air is blown. The **Huntington-Heberlein process** is perhaps the best known, and is very largely used. The crushed ore is first roasted with silica and limestone, most of the sulphide being converted into sulphate. After cooling, the charge is transferred to the converters, which are nearly hemispherical iron pots carried on trunnions, and in which a small fire is first lighted. As the layer of ore increases the blast is also increased, finally reaching to a pressure of about 16 ozs. per square inch. The whole mass gradually gets red hot and sinters; it is then tipped out, allowed to cool, and broken up. The chemistry of the process is not clearly understood. Desulphurisation is nearly complete, and very little lead sulphate is left. R. Tandler conveniently sums up the reaction thus—

$$PbS + CaO + 2O_2 = PbO + CaSO_4.$$

A similar process has been devised by Messrs. Carmichael and

Bradford of the Broken Hill Proprietary Company. The galena concentrates and slime are mixed in a pug mill with dehydrated gypsum and moistened with water. The mass solidifies owing to the hydration of the calcium sulphate, and is afterwards treated in converters exactly as in the Huntington-Heberlein process. The capacity of the blast furnace is very largely increased by the use of ores prepared in this way by either of the above processes. Still another method of preparing material for blast-furnace treatment is to convert it into briquettes, and this method is often practised.

The blast furnace used for lead smelting is of various forms, being either circular or rectangular in section, and is usually of nearly uniform diameter throughout its length. The lower part of the stack (bosh) is fitted with twyers, and is now always water-jacketed. The type used in Germany is known as the Pilz furnace, and is circular in section, about 25 feet in height, and 6 feet diameter. The stack is usually of masonry and the water-jacket about 20 inches high. The circular furnaces used in America are very similar, but somewhat smaller in diameter, and with much deeper water-jackets. Modern furnaces of a large capacity are nearly always rectangular, about 3 feet 6 inches wide, up to 12 feet long, and about 20 feet in height. The three essential portions of the furnace are (1) the hearth which receives the molten metal; it is built of firebrick lined with clay, and is abont 2 or 3 feet deep; as the metal must be kept melted, the hearth is not water-jacketed. (2) Above the hearth is the water-jacketed portion fitted with twyers. (3) The shaft or stack, usually made of iron and lined with firebrick, carried on girders supported on iron columns. The lower portion of a modern furnace is shown in the accompanying figure.

The hearth is always kept full of molten lead, which is drawn off continuonsly by means of a siphon tap. Suitable arrangements are made for drawing off matte and slag as they accumulate, and a separate forehearth is sometimes used for their separation, as described under copper (p. 246). In charging the furnace the materials are not mixed, but put in separate layers. The fuel used is generally coke, occasionally mixed with a little charcoal. Coal is seldom used. As a flux oxide of iron is nearly always required, and is best used in the form of hæmatite as free as possible from silica. Limestone may also be required, and this should also be as pure as possible. The furnaces are sometimes charged through the top and sometimes through side openings. Various devices are in use for automatic charging, and the cup and cone arrangement similar to that used in iron smelting blast furnaces is coming into more general use. The air-blast is supplied

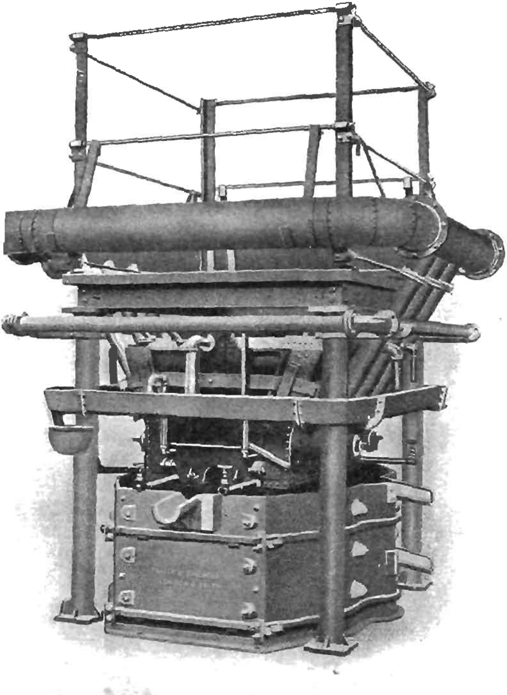


Fig. 38.—Lead smelting furnace.

at a *pressure of about* 3 lbs. *per square* inch, *and is cold*; a hot blast not having been found advantageous. The main reactions

which take place in the furnace have already been indicated. The lead present as oxide is reduced partly by carbon monoxide and partly by solid carbon; that present as sulphide is "precipitated" by iron which is formed by the reduction of ferruginous compounds added as flux. Any silicate present is reduced by carbon in the presence of ferrous oxide and lime, while lead sulphate is reduced partly by reaction with lead sulphide, or is converted to lead sulphide by carbon, and this sulphide decomposed by iron. The products of the above process are (1) impure lead or bullion which is further treated in the manner described below; (2) matte or regulus consisting chiefly of ferrous sulphide, and carrying with it copper sulphide and a portion of any zinc and arsenic that may be present in the ore; (3) slag consisting of a double silicate of iron and lime with silicates of other metals. The nature of this slag is very important in blast-furnace work; it must be sufficiently fusible and not too dense to allow of separation from the matte; the slag aimed at is almost always of the monosilicate type; (4) fume, the treatment of which has been considered above.

The products of the well-known Freiberg process—which is mainly notable for its highly systematic method of working, whereby the whole of the valuable constituents of the ores treated—viz., Pb, Zn, Bi, Ag, Au, As, $CuSO_4$, $FeSO_4$, $MnSO_4$, Ni, and Co as arsenides, As_4O_6, As_2S_3 and As_2S_2, are recovered —are similar to those mentioned above, a crude or "work-lead," a matte and a slag being produced, and occasionally a *speiss* rich in nickel, cobalt, silver, and arsenic. In these processes an alternate roasting to remove sulphur, and reduction of the resulting oxide, are the characteristic features, a fraction of the lead being obtained by each pair of operations.

For the treatment of mixed lead-zinc sulphide ores, see under Zinc, p. 291.

Treatment of Crude or Work Lead (*Werk-blei*).—The chief impurities in crude lead are antimony, copper, arsenic, bismuth, silver, and iron. An analysis of a Freiberg crude lead (from an arsenical ore) is as follows:—

	Per cent.
Lead,	97·72
Arsenic,	1·36
Antimony,	0·72
Iron,	0·07
Copper,	0·25
Silver,	0·59

Two of the most desirable qualities of lead are its softness and plasticity, properties which are impaired by the presence of impurities. Most of the impurities of lead (except silver, copper,

and bismuth) are more oxidisable than the metal itself. The process of **improving** or **softening** consists in exposing the molten lead to an oxidising atmosphere. The furnace used for the purpose is of the reverberatory type, with a hearth consisting of a wrought-iron or mild steel pan lined with firebrick. The hearth is generally water-jacketed at the sides to diminish the corrosive action of the oxides formed. The pig lead is melted, run into the pan, and allowed to remain in an oxidising atmosphere. The dross which rises to the surface is raked off from time to time, until a sample ingot of the lead shows a crystalline surface. The lead in the dross is recovered by reduction with coal, and is sufficiently rich in antimony to be sent to the type foundry. Copper, although less oxidisable than lead, forms a mixture with it which is less fusible than lead and sufficiently light to rise to the surface as the metal cools, and is skimmed off with the dross. Bismuth cannot be got rid of in the softening process, but is concentrated with the silver in the Pattinson process described later; it is usually present only in small amount. When the lead is rich in copper, it is advantageous to *liquate* it before improving. A liquation furnace is a reverberatory furnace with a hearth which slopes from the fire-bridge downwards, and terminates in a well. The pigs of lead are placed at the top of the slope, and the temperature so regulated as to little exceed the melting point of lead, which flows down into the well, leaving behind the less fusible impurities, such as copper—sulphur and arsenic being also partially separated in combination with the metallic impurities. The softening process is a necessary preliminary to desilverisation, because the impurities present interfere with both the Pattinson and Parkes processes.

Processes for Desilverising Lead.—The removal of silver from lead may be effected by taking advantage of the fact that lead is more easily oxidised than silver, as in the laboratory method of silver assay. Inasmuch as it is in this case necessary to subsequently reduce the lead oxide formed, such a process can only be profitable when the lead is comparatively rich in silver. This is the principle of the process formerly in use. It is now customary, however, to submit the argentiferous lead to a concentration process, whereby an alloy rich enough to be profitably oxidised by cupellation can be obtained. There are two distinct methods for this purpose in use.

Pattinson's process depends upon the fact that when a bath of argentiferous lead is allowed to cool gradually, crystals of lead poorer in silver than the rest of the bath first form. This condition obtains until the lead contains 600 to 700 ozs. of silver to the ton, when such spontaneous segregation ceases. So small a

quantity as 2 to 3 ozs. of silver to the ton of lead may thus be extracted, although the limit for profitable working depends on the market price of silver. The Pattinson plant (Fig. 39) consists of a series of cast-iron pans, holding 10 to 20 tons each, represented in the diagram. Each is heated by its own furnace. The lead to be desilverised is run into a pot near the middle of the series—*e.g.*, No. 5. The lead is kept melted for a short time, skimmed from dross, and is then chilled, sometimes by sprinkling water on the surface, and the cake of solidified lead broken up with a "slice" and stirred into the bath. The stirring is continued until $\frac{1}{3}$ to $\frac{7}{8}$ has solidified, according to whether the "high" or "low" system (*v.i.*) is being used. The crystals poorer in silver than the original lead are now fished out by means of a perforated ladle, *a*, working on the block, *d*, as a fulcrum, and transferred to pot No. 6, while the liquid portion is transferred to pot No. 4. A fresh batch of lead of the same

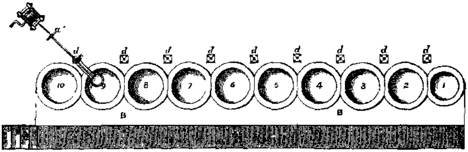


Fig. 39.—Plant for Pattinson's process.

content of silver as that previously used is run into pot 5, and the process repeated until pots 6 and 4 contain sufficient lead to allow of their contents being fractionated in the same way, the poorer lead of each fractionation going to the pot immediately to the left and the richer to the right.

It will thus be apparent that the extreme right-hand pot ("rich pot") will be continually receiving lead rich in silver, and the extreme left-hand pot ("market pot") is continually receiving lead almost completely desilverised—*e.g.*, containing only $\frac{1}{2}$ oz. Ag per ton, and ready to be cast into marketable pigs. It is obvious that as there is a regular gradation of content of silver throughout the series of pots, crude lead of any content of silver can be worked up together with another of a different content by starting each in its appropriate pot. In the high or $\frac{1}{3}$ system, the content of silver is approximately doubled at each separation. In the lower or $\frac{7}{8}$ system the increase of silver content

is about three fold at each step. The low system is particularly applicable to the treatment of comparatively rich lead.

The dross formed is worked up with lead slags in the manner already described. An incidental advantage of the Pattinson process is that it is an improving process apart from its use for desilverising. This results from the free exposure of the melted lead to the air. The double function causes the use of the Pattinson process in white lead making, where the purity of the lead is essential for success. In some cases a single pot is used, provided with draining grates and an inlet for steam. Repeated crystallisations are carried on as in a Pattinson battery of pots, steam at 50 lbs. pressure being admitted to take the place of hand stirring with a slice, and the still molten rich lead is tapped off, leaving the crystals on the grating. It is claimed that the steam equalises the crystallisation better than stirring does, and at the same time improves the lead by provoking limited oxidation. This modification is known as the *Luce-Rozan* process, and has been frequently adopted in place of the original method.

Parkes' Process.—This method is an example of the purification of a metal by extraction with an immiscible solvent. It depends upon the fact that fused lead and zinc are not miscible in *all* proportions, but each dissolves the other to a limited extent,* and that zinc alloys more easily with silver than does lead. Thus, when zinc is melted in a bath of argentiferous lead, a partially oxidised alloy of lead, zinc, and silver rises and solidifies, constituting a scum on the lead. The process is conducted in pots, a section of one of which is represented in Fig. 40. Contrary to the requirement of the Pattinson process, which is that the temperature shall be maintained at or near the fusing point of lead (325° C. = 617° F.), the bath in the Parkes process is kept somewhat above the melting point of zinc (415° C. = 779° F.) in order to ensure perfect admixture. The lead is charged into a pot, A, where it is melted; an ingot of zinc is then thrown on the surface, and when this is fused the rest of the zinc is added, the quantity necessary depending upon the richness of the lead in silver, and varying from $1\frac{1}{4}$ to 2 per cent., though in modern practice as much as 6 per cent. is often used. The whole is then stirred, either mechanically or by the admission of steam, in which case a high temperature must be avoided lest the steam oxidise the zinc. After the stirring has been continued for half an hour, the fire is damped down and the crust of zinc-lead-silver alloy, termed technically *zinc amalgam* (containing, for

* At 400° C. = 752° F., lead dissolves 0·8 per cent. of zinc; zinc, at its fusing point, dissolves 1·5 per cent. of lead.

example, Pb 55 per cent., Zn 40 per cent., Ag 5 per cent., mixed with oxide),* is allowed to solidify, and removed with a perforated ladle. The lead is then baled out or removed by the pump, B, which consists of an iron cylinder fitted with a valve, C, opening inwards, an exit tube, D, and a steam admission tube, E. The molten metal lifts the valve, C, and finds its level in the cylinder, B, being then driven by steam pressure up the exit tube, D, into the delivery tube, F, whence it flows into the pig mould, G. When the lead in the cylinder has all passed over, the pressure of steam is automatically relieved through the exit tube, D; lead again flows into the cylinder, and the process is repeated, the emptying action being almost continuous. The removal of the small quantity of zinc which remains dissolved in the lead is a difficulty of the process, and several methods have been adopted. Treatment in an improving furnace (*v.s.*) has been

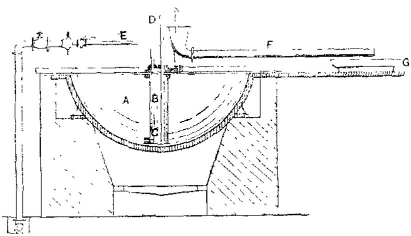


Fig. 40.—Plant for Parkes' process.

A, Melting pot; B, pump; C, valve; D, exit tube; E, steam admission tube; F, delivery tube; G, pig mould.

used. Another plan consists in stirring the zinciferous lead with lead chloride which converts the zinc into $ZnCl_2$, an equivalent of lead being reduced. Steam may also be used to oxidise the zinc, or an oxidising fusion in a blast furnace may be adopted.

The zinc alloy skimmed off is first liquated to remove most of the lead. The lead goes back to the Parkes pots, and the remaining alloy (Zn and Ag) is heated in a graphite distillation crucible (see *Zinc*), together with wood charcoal, zinc from the

* It is claimed that the presence of a small proportion of aluminium (0·5 per cent.) in the zinc used will much diminish the proportion of oxide in the alloy.

alloy and from the oxide being thus recovered.* The residue is then worked up for silver (*q.v.*). The Parkes process has largely replaced the Pattinson process except for the manufacture of "chemical lead" (*e.g.*, for lead sheets for sulphuric acid chambers), for which lead containing traces of zinc is not suitable. At some works—*e.g.*, at Freiberg—the Pattinson and Parkes processes are combined, the former being used until the rich lead contains only 50 ozs. of silver per ton, when it is treated by the latter.

The subject of cupellation—*i.e.*, the separation of silver when present in considerable amount from lead, by the oxidation of the latter, will be dealt with under *Silver*.

Electrolytic Winning and Refining of Lead.—It is not probable that a successful method of winning lead from its ores by means of electrolysis will be devised. An attempt has been made at Niagara Falls to reduce galena electrolytically to spongy lead. The crushed galena was placed in a number of shallow saucers made of antimonial lead. These saucers, insulated from each other by rubber rings were piled in the form of a column in a vessel containing dilute sulphuric acid as the electrolyte. The whole set was run in series, the outer surface of the bottom of each pan being a cathode and the galena itself an anode. The arrangement is represented diagrammatically in the figure.

The cathode product, spongy lead, was washed free from gangue, and used either for accumulator plates or for the production of red lead or litharge. Other attempts have been made to electrolyse fused galena. E. F. Kern has patented a process in which the electrolyte is lead chloride (fusing at 500° C.) saturated with lead sulphide. Galena is fused and cast into anodes. The reduced lead is said to be malleable and free from sulphur.

Attempts to refine crude lead electrolytically have met with a qualified success. When lead is rich in silver (*e.g.*, contains as much as 180 ozs. per ton) it is said to be capable of profitable refining by electrolysis. For this purpose, thin plates of the lead are enclosed in sacking and serve as the anode of an electrolytic cell charged with a solution of lead sulphate in sodium acetate heated to about 40° C. = 104° F. The cathodes are of pure lead. The lead deposited on these soon strips off and falls to the bottom of the bath. When the anodes have nearly dissolved, the gold

* Electrolytic refining of the alloy has been attempted. The alloy is cast into slabs to serve as anodes, from which the zinc is to be electrolytically dissolved and re-deposited, leaving the silver and lead. It is, however, difficult to deposit zinc electrolytically from any but an alkaline bath.

and silver which have collected in the bags may be worked up. The lead need not be "improved" previous to refining. This process, due to Keith, has been modified by Tommasi. The cathode is a large disc of copper or aluminium bronze which revolves between the lead anodes, and is only partly immersed in the electrolyte. The latter is a solution of lead acetate in *sodium or potassium acetate. The freshly deposited lead is* scraped off the revolving disc mechanically, collected in gutters, and afterwards treated.

Neither of these *processes is used commercially. The most* promising method of refining lead electrolytically is that due to Betts, in which a solution of lead in hydrofluosilicic acid forms the electrolyte. Lead is readily precipitated from such a solution, and if gelatin be added the metal is obtained in a compact form. *To prepare the electrolyte hydrofluoric acid* of 35 per cent. strength is converted into hydrofluosilicic acid, H_2SiF_6, by filtering through a bed of quartz. White lead is then added,

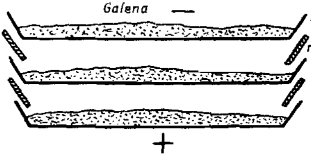


Fig. 41.

any sulphuric acid present being precipitated as lead sulphate. The filtered solution contains about 8 per cent. of lead and 15 to 16 *per cent.* of H_2SiF_6. *In addition, 400 to 500 grammes of* gelatin are used for every ton of lead deposited, being added from time to time as a solution in hot water. The lead to be refined is cast into anodes of suitable size. The cathodes are thin sheets of steel covered with non-adherent coats of lead. Electrolysis is carried out at a temperature of 30° to 35° C., the electrolyte being circulated from vat to vat, avoiding exposure to the air as far as possible. Each vat or wooden tank contains 22 to 28 anodes and 23 to 29 cathodes. In future cement vats will be used. A large part (one-quarter to one-third) of the anodes is converted into sludge which is periodically removed, washed, and treated in a reverberatory furnace, a very fusible antimonial lead oxide being obtained, besides metallic lead containing the precious metals and any bismuth, and an argentiferous

copper slag. Most of the arsenic present is volatilised. The method is being used at Newcastle and in the United States, its chief advantage being its small loss of lead and comparatively large recovery of other metals present.

Uses of Lead.—For the use of lead as a structural material, for its employment to resist mineral acids (*e.g.*, in vitriol chambers) and for the manufacture of paints, see the sections allotted to these subjects, Vol. II. Large quantities of lead are also used for the plates of electric accumulators.

Commercial lead is one of the purest metals industrially prepared, as may be seen from the following analysis :—

Lead,	99·9837	per cent.
Copper,	0·0014	,,
Antimony,	0·0037	,,
Zinc,	0·0016	,,
Iron,	0·0016	,,
Silver,	0·0080	,,
	100·0000	,,

Most of the impurities of lead tend to harden it. The specific gravity of the pure metal is 11·35, and the melting point is 325° C. = 617° F.

Lead Alloys.—The principal alloys of lead are those with tin, antimony, and arsenic. The term "white metal" has been applied indiscriminately to alloys of lead, antimony, and tin, or any two of these metals.

Lead and tin do not form compounds but mix in all proportions. An eutectic is formed containing 37 per cent. of lead, and having a melting point of 180° C. The lead-tin alloys have a greater tenacity and are more fusible than either metal. Thus **pewter** (20 per cent. Pb, 80 per cent. Sn) is a strong alloy not easily corroded, the safety of which for drinking vessels is impaired if the proportion of lead be sensibly increased. Common **solder** (tin solder) consists of equal weights of lead and tin: plumber's solder 2 parts by weight of lead to 1 of tin (see p. 43). Fine solder has the composition 2 of tin to 1 of lead. These alloys have a lower fusing point than either constituent has—*e.g.*, common solder melts at 190° C. = 374° F.—but the fusing point rises with the percentage of lead when the proportion 1 of lead to 2 of tin has been exceeded. The suitability of these alloys for soldering purposes is due to the fact that they have two points of solidification, one for the eutectic alloy contained and another for the excess of free metal present. Between these two points the alloy remains in a pasty condition suitable for the plumber's use.

Lead and antimony also mix in all proportions without forming compounds, the eutectic in this case containing 13 per cent. of antimony with a melting point of 228° C. The framework of accumulator plates is generally made of lead containing up to 4 per cent. of antimony.

Pure lead-antimony alloys are, however, little used, as they are not sufficiently strong. To increase their strength tin is added; this forms a hard compound with antimony possessing the formula SbSn. The alloy is then composed of these hard particles embedded in a softer matrix, a condition which makes for mechanical strength. **Type metal** contains 70 per cent. of lead, 18 per cent. of antimony, 10 per cent. of tin, and 2 per cent. of copper. **Stereotype metal** has 82 per cent. of lead, 14·8 per cent. of antimony, and 3·2 per cent. of tin. The function of the antimony in these alloys is to produce a metal hard enough to withstand the pressure of the printing machine. **White metal** (*antifriction metal*) is also lead hardened with antimony, and containing tin—*e.g.*, 75 per cent. Pb, 15 per cent. Sb, 10 per cent. Sn. Antimony may vary from 10 to 18 per cent., but should not exceed the latter figure or the alloy will be brittle. **Magnolia metal** is a similar alloy, containing, in addition, about 0·2 per cent. Bi. For making shot for sporting guns, lead is slightly hardened by arsenic, which also appears to favour the assumption of sphericity by the drops of melted metal as they fall down the shot tower. They are commonly blackened by reception in a solution of sodium sulphide, or by tumbling with graphite. On account of the low fusing point and plasticity of lead, it can be formed into rod and tube by forcing it, while just at its melting point, through a die, plain for rod and cored for tube. To obtain a harder tube than is afforded by pure lead (*e.g.*, "compo." tube) some antimony is commonly added. The analyses set forth above are only given as indicating the general nature of these alloys, the composition of which varies widely.

ZINC.

Zinc does not occur native. Its chief ores are as follows :—

1. **Blende** (*zinc sulphide*, ZnS).—This mineral occurs associated with sulphides of lead, iron, and copper; it is usually black (whence the mining name "black-jack"), from the presence of these impurities, and lustrous. It is the chief source of the metal. Good ordinary samples contain about 50 per cent. Zn; pure ZnS contains 66 per cent. Zn. It often contains cadmium sulphide.

2. **Calamine** (zinc carbonate, $ZnCO_3$).—This is also coloured by iron, frequently being brown, from the presence of ferric oxide. It may contain about 40 per cent. of zinc instead of 52, which is the theoretical percentage. An ore consisting of hydrated oxide and carbonate, $ZnCO_3 \cdot 2Zn(OH)_2$, is also worked.

3. **Zinc Silicates.**—The most abundant of these is *electric calamine*, $Zn_2SiO_4 \cdot H_2O$, so called from the fact that it is said to become electric on heating. It is usually white. It is often confounded with calamine, which it resembles in physical properties. *Willemite*, Zn_2SiO_4, is another zinc silicate which is worked.

4. **Red Zinc Ore** (zinc oxide, ZnO) owes its colour to the presence of oxides of manganese and iron. It may contain as much as 75 per cent. of Zn. It is seldom found alone, but is usually disseminated through Franklinite.

5. **Franklinite,** $(ZnFeMn)O + (FeMn)_2O_3$, may be regarded as magnetite in which ferrous oxide is partly replaced by zinc oxide. The iron is also associated with manganese, to which the peculiar colour of the mineral is due. Very large deposits are found in New Jersey.

The chief zinc-yielding districts are Belgium and the Rhine country, Silesia, Greece, France, United States, and this country, though the amount obtained here is comparatively small, Cumberland, Wales, and the Isle of Man being now the chief districts of supply. Zinc and lead ores are frequently found together and worked in concert, notably in New South Wales.

The **winning of zinc** differs from that of the metals already considered, chiefly in the fact that the volatility and heat of combination with oxygen of zinc are greater than those of these other metals (Fe, Cu, Pb). The boiling point of zinc is about 930° C. = 1,706° F., and its vapour is capable of reducing water vapour and carbon dioxide, properties which prevent its being smelted in a blast furnace. It is sometimes, however, feasible to treat ores of zinc in a blast furnace, but only as a means of obtaining a pure oxide; the metal is reduced in contact with the solid fuel of the furnace, volatilised, and burnt again to oxide by the exit gases; the oxide is then collected and reduced in the ordinary way (*v.i.*). The reduction of zinc oxide by means of solid carbon is represented by the equation—

$$ZnO + C = Zn + CO.$$

The decomposition of ZnO absorbs 85 Cal., whilst the formation of CO evolves 29 Cal. Thus the above reaction is endothermic to the extent of 56 Cal., which quantity of heat has to be supplied

through the walls of the retort in which the reaction is carried out.

Zinc ores are usually subjected to some preliminary process of concentration. The ore may be broken by hand or by means of jaw-crushers. The methods of separation include hand separation, gravity separation, magnetic separation, and flotation separation. The process often involves repeated crushings and siftings through cylindrical trommels, etc., into various sizes, each size being separately treated by a gravity process, either wet or dry, by means of jigs, table concentrators, etc. As regards magnetic concentration, the Wetherill machine is perhaps most generally used. For the discussion of the above methods, and of the subject of flotation concentration, see p. 168, *et seq.*

The next step in the treatment of the ore, whether it be blende or calamine, is the roasting of it to oxide. When calamine (zinc carbonate) is treated, it may be roasted, like limestone, in running kilns (see *Lime*), or in reverberatory furnaces; the object of the roasting is to avoid the presence of CO_2, which would oxidise the zinc in the retort in the subsequent distillation process. When blende (zinc sulphide) is roasted, much of it is converted into zinc sulphate, which can only be decomposed at a temperature considerably above that necessary to convert the sulphide into oxide. To avoid the formation of zinc sulphate as far as possible the blende is coarsely crushed and the roasting is conducted in shaft or reverberatory furnaces. More recently large mechanical furnaces have been used, these being either revolving furnaces, long-bedded furnaces with mechanical stirrers, or muffle furnaces (see under *Copper*, p. 242). A shaft furnace is sometimes used for a preliminary roasting. If the ore is in the form of a powder a reverberatory furnace is used. When the gases given off are to be used for the manufacture of sulphuric acid, kilns of the Gerstenhofer type or muffle furnaces are used, the latter yielding gases rich in sulphur dioxide, besides calcining the ore thoroughly. The roasted ore contains very little zinc sulphate, and, according to Voigt, is free from zinc sulphide, most of the residual sulphur being present as sulphates of lead and calcium, and as calcium sulphide. A considerable quantity of fume is obtained during the roasting; this contains some 10 per cent. of zinc as sulphate, which is leached out and precipitated as zinc carbonate.

The finely-ground calcined ore is mixed with about half its weight of powdered coke or non-caking coal, and the mixture is charged into retorts. These are of two forms, known respectively as the Belgian and the Silesian retort. The former, marked

a in Fig. 42, are fireclay tubes, either circular or elliptical in section, about 4 feet long, 8 inches internal diameter, and 1 inch thick in the walls; these are set in an inclined position (to facilitate charging and discharging) above the grate of a solid fuel furnace, or in a producer-gas furnace usually working regeneratively, similar to that used in steel-making (p. 197). The capacity of

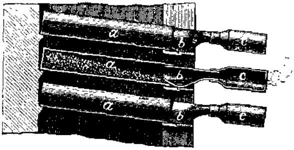


Fig. 42.—Belgian zinc retort.
a, Fireclay tubes; *b*, clay receiver; *c*, pot.

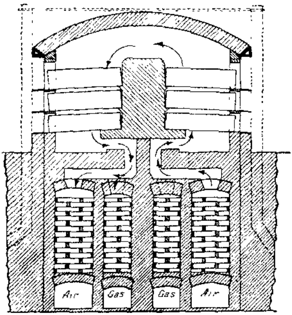


Fig. 43.—Three-tier Siemens-Belgian zinc furnace (Ingalls).

the furnaces varies considerably. Coal-fired furnaces may take 18 or more retorts arranged in six to nine rows. In gas-fired furnaces only three to five rows are used, but these are much longer, and may contain from 50 to 70 retorts in each row. The furnaces may be built singly or arranged in pairs or groups of

four. A modern three-tier Belgian furnace working regeneratively is shown in the accompanying figure.

The charge for a modern Belgian retort is about 63 lbs. As soon as the retorts are charged they are fitted with the clay receivers, *b*, which are from 16 to 24 inches long. When the temperature is sufficiently high, reduction commences, and after a time metallic zinc begins to volatilise. Conical sheet-iron condensers, *c*, each provided with a small hole for the exit gases, and about 30 inches long, are then attached to the clay receivers.

The latter (Silesian retorts) consist of ◠-shaped muffles, 4 to 6 feet long, 8 inches wide, and 18 inches in height, each taking a charge of about ¾ cwt. Modern retorts are often larger, and hold as much as 2 cwts. of ore. The front part of the muffle, A (Fig. 44), is fitted in its upper half with a clay nozzle, *p*, which

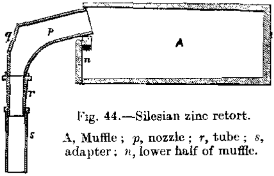


Fig. 44.—Silesian zinc retort.

A, Muffle; *p*, nozzle; *r*, tube; *s*, adapter; *n*, lower half of muffle.

is connected with the clay tube, *r*, leading into the sheet-iron adapter, *s*; the lower half of the front of the muffle, *n*, can be removed for the introduction of the charge; the muffles are set in rows, back to back, in a furnace with a long central grate, or are heated by producer gas with a regenerator in the usual way.

The details of modern Silesian furnaces vary somewhat. The condensers themselves may be kept within the furnace proper, only the iron "prolongs" being seen outside. The latter sometimes communicate, at their upper ends, with condensing chambers to retain the last traces of zinc. Other forms of condensers are also in use; the Dagner condenser, for instance, consists of a series of clay boxes through which the distillate is made to pass.

The receivers which are to collect the zinc must be of a temperature to keep it fused. The progress of the distillation is judged by the appearance of the issuing gases. Brown fumes of cadmium oxide first appear, and then zinc vapour, the uncondensed portion of which burns at the end of the condensers until the distillation is complete. Much grey, partially oxidised, and finely-divided zinc collects in the sheet-iron adapters; this is

marketed as **zinc dust** for use as a reducing agent. Usually, however, this dust and other residues containing zinc is mixed with ore and coke, the charge put into retorts in the cooler parts of the furnace, and redistilled. The yield of fused zinc, or **spelter,** as it is commercially termed, is from 70 to 80 per cent. of that in the ore.

In the Belgian process the sheet-iron adapters are emptied three or four times daily, the zinc which has accumulated in the clay condensers being ladled out at the same time. In both the Belgian and Silesian methods the retorts are discharged every twenty-hour hours, for which purpose steam is sometimes used in America.

A combination of the Belgian and Silesian methods is largely employed in Rhenish Prussia and elsewhere, the furnaces being often known as "Rhenish furnaces." Three rows of elliptical retorts are commonly used, the bottom row being supported throughout their whole length upon the hearth, as in the Silesian method, while the upper rows are supported at their ends only. The furnaces are usually gas-fired, the air necessary for combustion being pre-heated by means of the heat of the waste gases.

Refining of Zinc.—Crude zinc constantly contains lead—*e.g.*, 1 to 3 per cent.*—and often traces of arsenic, cadmium, and iron. It is refined by melting on a hearth provided at one point with a well, in which the lead settles out in the course of two or three days as a heavy lead-zinc alloy, this metal being but sparingly soluble in zinc (see p. 280). Above this comes a thin layer of highly ferruginous zinc, while the top metal is comparatively pure zinc. The latter is ladled out and cast into ingots. The hard ferruginous spelter is sold to makers of copper-iron-zinc alloys. The liquated lead contains 2 to 5 per cent. zinc, and is used for desilverising and other purposes. In America, where natural gas-fired furnaces are used and smelting costs are low, spelter is frequently refined by redistillation, but the product still contains 0·25 per cent. lead. Electrolytic methods of refining have been tried, but have not been found commercially successful.

Commercial zinc usually contains arsenic; this may be removed by adding 0·2 per cent. of metallic sodium to the fused metal, skimming off the surface layer and then granulating the metal by pouring into water. The scum contains practically the whole of the arsenic as a sodium-zinc compound, which appears to be most stable at a temperature near the melting point of zinc.

This refining is necessary for zinc that is to be rolled, as well as for that which is to be used for brass making. It is stated

* Lead is somewhat volatile in presence of zinc, and, therefore, distils over with the latter in the reduction process.

that the malleability is not affected provided the lead be below 1·5 per cent., but is much reduced by 0·25 per cent. of iron. Zinc that has been overheated and contains oxide is also unsuited for rolling.

Fume Filtration.—This process, which has a promising future, has for its primary object that of obtaining zinc free from lead as a product when smelting zinc materials containing lead. Briefly, the method is to insert between the retort and the condenser a short clay tube containing refractory material through which the vapours are "filtered" before condensation. The original idea was to detain the intermingled impurities by some chemical reaction. In the Hopkins' process carbon is used for this purpose. This may possess an advantage over other materials (which are also used), inasmuch as, in an incandescent state, it helps to maintain a reducing atmosphere. The action, however, appears to be essentially mechanical, the heavier constituents of the mixed vapours being sufficiently retarded in their course of diffusion to effect a more or less complete separation from the lighter, which pass on in an almost pure condition. As a result a very pure spelter is obtained, and the lead partially recovered in the metallic form. There is a tendency, also, to obtain higher yields. The process is now being used for obtaining almost pure spelter (containing 99·86 per cent. Zn) from such crude materials as galvanisers' "dross," zinc ashes, etc., and in the future will doubtless be applied to the direct distillation of ores and lead-zinc concentrates. By fitting a similar nozzle or filter to the outer end of the condenser the escape of "zinc fume" into the atmosphere is said to be almost entirely prevented.

Treatment of Mixed Sulphide Ores; Electrolytic Winning of Zinc.—Large quantities of complex lead-zinc sulphide ores exist in New South Wales and various parts of America which do not lend themselves readily to ordinary smelting methods. An elaborate system of concentration yields five products, four of which can be smelted, with more or less success, for lead and zinc. The largest proportion, however, is the "middlings," the treatment of which is one of the most difficult of metallurgical problems. This problem is one of the chief causes of the various attempts which have been made to devise a workable wet or electrolytic method of extracting zinc. A possible solution of the difficulty has been mentioned in connection with "fume filtration," briefly considered above, but this remains to be seen. In some of the dry processes which have been devised (*e.g.*, the Bartlett process) the middlings are reduced with coke, the zinc volatilised and condensed as a fume consisting largely of zinc oxide and basic lead sulphate; this powder is sold as a white-

lead substitute. In other processes the ore is roasted, fluxed with alkalies in a blast furnace, and the zinc obtained as a slag. The latter is then smelted with coal in a basic-lined Siemens furnace, the zinc volatilised and collected as oxide. A very large number of wet methods have been suggested, all based on similar general principles, and which it is unnecessary to consider in detail. In almost all of them the ore is roasted either alone, so as to convert the zinc into sulphate or oxide, or with salt, so as to convert it into a mixture of chloride and sulphate. The zinc is then leached out (by suitable solvents) and precipitated as oxide or carbonate, iron and other metals being first removed by suitable means, if necessary for a white product to be obtained. Various leaching agents have been proposed, such as water, dilute acids, ammonium salts, and ferric chloride, while suggested precipitants for the zinc include lime, sodium sulphide, and sodium carbonate. In addition, there remains the treatment of the argentiferous lead residues. None of these processes can be said to have solved the problem of the treatment of complex sulphide ores.

The **Siemens-Halske process** is a combined wet and electrolytic process. The ore is roasted at a low temperature and the zinc converted largely to sulphate. It is then extracted with dilute sulphuric acid, foreign metals precipitated by suitable means, and the faintly acid solution of moderately pure zinc sulphate electrolysed between lead anodes and zinc cathodes. Sulphuric acid accumulates in the solution, which is again used for leaching purposes. The difficulty of preparing a pure zinc sulphate solution, and of keeping the electrolyte sufficiently pure militate against the success of this method. In another Siemens-Halske process the unroasted ore is treated with chlorine and leached; the residues are smelted and the solution is electrolysed. Chlorine is liberated and is used again.

The **Ashcroft process** was also designed to treat mixed sulphide ores. The latter were roasted and leached with ferric chloride solution, the residue being smelted for lead. The solution was electrolysed first between iron anodes and zinc cathodes, by which part of the zinc was precipitated and ferrous chloride formed; then between carbon anodes and zinc cathodes, where most of the remaining zinc was precipitated, ferrous chloride being also oxidised to ferric chloride, which was used again for leaching. The failure of this method led to the **Phœnix process** being devised. The fundamental reaction in this process consists in attacking the sulphides with chlorine at a low red heat in a vessel resembling a converter, tapping off the mixed chlorides, selectively precipitating the chief metals other than zinc, and

finally obtaining a solution of zinc chloride approximately pure. This solution is boiled down and the zinc chloride electrolysed in the fused state between anodes of carbon and cathodes of fused zinc, the electrolyte being kept fused by the current.

Numerous processes for the electrolytic winning of zinc have been devised by **Hoepfner.** In one modification the ore, after roasting for sulphur, is mixed with 20 per cent. of salt, and again roasted to chloridise the zinc. The solution obtained by extracting the roasted mass is cooled to $-5°$ C. $= 23°$ F. to separate the sodium sulphate formed during roasting, and the solution of zinc chloride is electrolysed in cells provided with diaphragms of nitrated cotton. The anodes are of carbon, and the cathodes are rotating zinc discs, the electrolyte being kept fairly strong in order that a coherent deposit may be obtained. This process has been worked on a commercial scale. Another **Hoepfner process** is being worked in this country by Brunner, Mond & Co., and is very similar to that just described. The zinc chloride is obtained by acting on zinc oxide (roasted zinc ore) with calcium chloride solution and carbon dioxide, calcium carbonate being produced. This reaction is said to work smoothly. The real object of the alkali maker is to recover chlorine from his waste calcium chloride liquors.

Mond has devised the following apparatus to overcome the difficulties experienced in obtaining a good adherent deposit of zinc. The cathode consists of not fewer than three long rotating mandrels, the bearings of which are arranged in such a way that horizontal motion is permitted. These cylinders are kept pressed together by means of springs, and are slowly rotated in the electrolyte. To prevent the same parts of the cylinders from coming in contact too frequently the cylinders are all of different diameters, and to give the deposit a good burnish a slight sliding motion is imparted to one of the mandrels whilst rotating. The deposited zinc is removed as tubes from the mandrels and cast into ingots in the usual way.

Within recent years attempts have been made to distil zinc in the electric furnace. Dorsemagen has proposed to heat a charge of calcined siliceous zinc ore and coal in a furnace of the crucible type with vertical electrodes. Zinc is said to be reduced and volatilised and silicon carbide left behind; in the presence of iron ferro-silicon is formed.

During the last few years zinc has been produced on a commercial scale in Germany and Sweden (with exceptionally cheap water power) by electrothermic smelting in the **De Lavel furnace.** Fig. 45 shows the form of furnace and method of heating employed by De Lavel. The finely-divided zinc ore is mixed

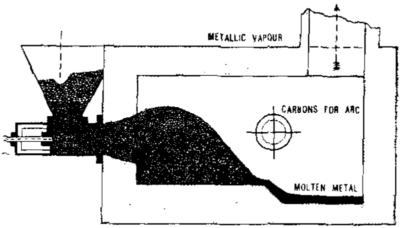


Fig. 45.—De Lavel electric furnace for zinc.

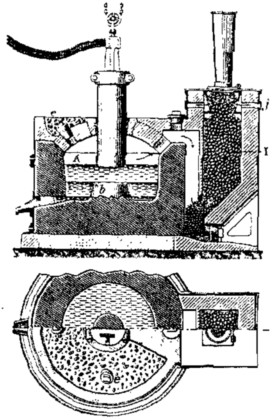


Fig. 46.—Côte-Pierron zinc furnace.

with powdered coal, limestone, and other fluxes, and is then submitted to the radiant heat of an electric arc in the form of furnace shown in sectional elevation in the figure. By careful

regulation of the distance of the arc from the ore and fluxing materials at the charging end of the furnace the purity of the product can be controlled at will. Details of the apparatus and arrangements for condensing and separating the metallic vapours are not available. The product is stated to be remarkably pure, containing 99·9 per cent. of zinc. The furnace has been used chiefly for refining raw spelter.

A recent process for smelting zinc in the electric furnace is the **Côte-Pierron process,** which consists in reducing zinc sulphide by means of iron. The furnace adopted on a commercial scale is shown in the illustration.

The lower part of the crucible, A, with the projection, *b*, is made of graphite, and is connected with one pole of the electric circuit. The roof is formed of refractory firebrick, and is provided with openings, *e*, for the introduction of the charge. The zinc vapours pass into the condenser, I, containing carbon. Air is admitted through the opening, *j*, to raise the falling carbon to a red heat, so that at a point lower in the condenser the zinc "mist" may be reduced. The furnace is also used for the manufacture of zinc oxide by passing the zinc vapour to a combustion apparatus and collecting the oxide in settling chambers. For the production of commercial white zinc oxide, free from iron, the reaction of lime and carbon with zinc sulphide is utilised, a graphite crucible being employed—

$$ZnS + CaO + C = CO + CaS + Zn.$$

The zinc oxide obtained contains 98·6 to 99·0 per cent. ZnO and 0·2 to 0·3 per cent. of iron.

Uses of Zinc.—The specific gravity of zinc is 7; its melting point is 419° C. = 786° F. At the ordinary temperature it is brittle, but between 110° C. and 150° C. it is malleable, so that sheet zinc can be prepared at this temperature, and is much used for pipes, gutters, etc., for which it is more advantageous than iron, both on account of its somewhat lower specific gravity and its greater resistance to corrosion. Other uses for sheet zinc include its suspension in boilers to prevent corrosion, and for gold extraction by the cyanide process. The printing trades also use zinc extensively for "process" blocks. The use of zinc for coating iron has been already dealt with (p. 30). Zinc white is made directly from zinc by burning it (see *Pigments*, Vol. II.), and crude spelter is used, with sulphuric acid, as a cheap source of hydrogen. The application of the metal in primary batteries has been already explained (p. 117); also for desilverising lead (p. 280). Zinc chloride is used for mercerising cotton, while zinc sulphate is used in dyeing and calico printing.

Zinc Alloys.—Brass has already been considered under copper; the zinc used for making it should be as pure as possible. *Zinc-iron alloys (Zinceisen)* may be prepared by immersing clean iron sheet in a bath of zinc heated to near its boiling point, and are also obtained as bye-products in zincing (*galvanising*, p. 30). They are used as convenient means for introducing iron into special copper-zinc alloys, such as Delta and Bull metal. Zinc-antimony alloys are used for thermopiles. The behaviour of zinc-lead alloys has been dealt with under the desilverising of lead by the Parkes process. Zinc-aluminium alloys are now important industrially (see p. 353). For German silver see p. 317.

CADMIUM.

Cadmium occurs as *Greenockite*, CdS, a somewhat rare mineral of no commercial importance. The metal accompanies zinc in almost all specimens of its ores, and distils over during the first two hours of zinc distillation as "blue powder" containing 1 to 8 per cent. of cadmium. The bulk of the cadmium of commerce has been prepared from this product by a process of fractional distillation. The powder is mixed with coal and distilled at a low red heat from cast iron or clay retorts having long sheet-iron cones as adapters. The enriched distillate may contain over 20 per cent. of cadmium, and is redistilled until a product containing 99·5 per cent. of cadmium is obtained, affording an illustration of the general applicability of fractional distillation. Lately considerable quantities of cadmium have been obtained as a bye-product from the manufacture of lithophone (see Vol. II.). In the preparation of the latter the impure zinc solutions are purified by boiling with zinc dust which precipitates foreign metals, chiefly cadmium, after iron and manganese have been removed. In a new process at Marienhütte (Upper Silesia) the crude solutions are subjected to electrolysis in lead-lined tanks, zinc anodes being suspended in the liquor. The zinc dissolves in the neutral solution, while foreign metals are deposited as slime on the lead lining which serves as cathode. The mud may contain from 30 to 70 per cent. of cadmium, and from this it is possible to prepare crude cadmium, which then serves as an anode in the electrolytic separation of the commercial cadmium. The metal appears in commerce in the form of sticks.

Cadmium is a metal standing in many respects between zinc and lead. It is soft enough to mark paper faintly. It melts at 321·7° C. = 612° F., boils at 778° C. = 1,432° F., and has a specific gravity of about 8·6.

Uses of Cadmium.—The metal is employed in the preparation

of certain alloys of low melting point (fusible metals), such as "Woods' metal" (see *Bismuth*, p. 309). Silver dissolves cadmium to the extent of 20 per cent., forming a homogeneous solid solution. Plating with an alloy of silver and cadmium has been practised, and is said to have the advantage that the coating is not so easily tarnished as pure silver. Cadmium is used extensively for making silverware, owing to its valuable properties as a deoxidiser. It is usually added to the extent of 0·5 per cent., and imparts malleability, prevents blisters, and is said to improve the whiteness of the metal. At normal prices cadmium is much used for cadmium plating; on tin the coating is very hard, and takes a high polish. Alloys of tin and cadmium containing 20 to 30 per cent. of the latter are now used for anodes in electro-plating the interior of telephone parts in place of nickel. Alloys of cadmium with gold, silver, and copper are easily fusible, and are used for jewellery. With zinc and tin cadmium forms alloys which are used as solders for aluminium and aluminium-bronze. Cadmium also serves as a basis for cadmium yellow, CdS, which is used as a pigment (see Vol. II.), and in pyrotechny.

TIN.

Tin does not occur native. The following are its ores :—

Tinstone or **Cassiterite.**—This ore consists of crystals of stannic oxide (SnO_2), generally occurring as masses in lodes, or disseminated in very small veins through granitic rock. The denudation of the rocks carrying tinstone has given rise to alluvial deposits of the ore in sands, the ore being then known as *stream-tin*. Arsenical pyrites, wolfram, and other minerals accompany the siliceous gangue of the tinstone. Tinstone is sometimes found light in colour, of regular crystalline form, and approximately pure, but is generally dark from the presence of oxides of iron and manganese. Considerable quantities of tinstone are still raised in Cornwall and Devon, but the islands of Banca and Biliton, the Malay Peninsula, Australia, and Bolivia furnish the chief supplies.

Tin pyrites is essentially a triple sulphide of tin, copper, and iron, containing about 26 per cent. of tin, 30 per cent. of copper, 12 per cent. of iron, and 31 per cent. of sulphur. Zinc and other metals are sometimes present. This ore is of minor importance, and generally accompanies cassiterite to some slight extent.

THE WINNING OF TIN.—1. **Preparation of Tin Ores.**—The majority of tin ores are comparatively poor, containing, for example, 1 to 2½ per cent. of metallic tin, and a cheap method

of mechanical concentration is, therefore, necessary. Such a method is rendered possible by the fact that the specific gravity of tinstone (6·5) is much higher than that of most of the accompanying gangue (the specific gravity of quartz being 2·7), so that by stamping the ore (see *Gold*) and washing the resulting powder by a stream of water, the lighter gangue is carried further away by the water than is the heavier tinstone. Various types of concentrators are in use for the treatment of the crushed ore. Of these the Frue vanner, in which the ore is washed by a stream of water on an endless belt moving upwards, and the Wilfley table, in which the ore is washed on a vibrating table provided with riffle bars, are perhaps the most largely used. When the ore contains a good deal of pyrites, as is usually the case, the washing will not serve to remove the pyrites because the specific gravity of this mineral (5·0) is too near that of tinstone. The first concentrate—*i.e.*, the portion heaviest and richest in tin—must, in this case, be roasted in order to convert the sulphides into oxides, and thus reduce the specific gravity of the matter other than tinstone, the washing being then repeated. As in all methods of mechanical concentration, "sizing" of the ore before washing is advantageous, since effective separation is only obtained when the material treated consists of fragments fairly uniform in size (see *Gold*). Another object of this roasting is the removal of arsenic and sulphur, the former being condensed in a series of chambers, and forming the main source of "white arsenic" (*q.v.*).

Modern roasting plant, such as the Oxland and Hocking roaster, consists of a long cylinder slightly inclined towards a grate, the products of combustion from which traverse the cylinder from end to end. The cylinder is slowly revolved and ore fed in at the upper end, being roasted in its passage and falling out at the other end of the cylinder. The upper end of the cylinder opens into condensing chambers for the collection of arsenious oxide. Other types of furnace, as described under *Copper* (p. 242) may also be used for roasting. Before concentrating a second time the roasted material is now frequently treated by magnetic concentration. The material is made to travel on an endless belt under a series of other belts running at right angles to the main belt, and behind which magnets are arranged sufficiently strong to attract magnetic particles, which are then carried away by these transverse belts. The first belt serves to remove magnetic oxide of iron, and the second belt, provided with stronger magnets, removes wolfram. Each of the products may be subjected to further treatment; usually the tinstone thus separated is ready for the smelter. When the ore

is sufficiently rich in copper to pay for the process, the roasted ore is washed with dilute acid and the copper precipitated by iron (see *Copper*). Should bismuth be present it is, at the same time, dissolved by the acid (which in this case is hydrochloric acid), and is precipitated by dilution as basic chloride. As stated above, tungsten in the form of *wolfram* (a tungstate of iron and manganese) is sometimes present in tin ores, and on washing is left with the tinstone. This may be removed by fusion with a small quantity of soda ash (Na_2CO_3), whereby the tungsten is converted into sodium tungstate (Na_2WO_4). This may be leached out with water, together with a quantity of sodium stannate, corresponding with the excess of soda ash used. Sodium tungstate has a limited application in dyeing and for rendering light fabrics uninflammable. This process for removing tungsten is somewhat expensive, and is but little used. The purified tinstone has to be further washed to remove the ferric oxide left by the decompositiou of the wolfram.

2. **Reduction to Metallic Tin.**—Stannic oxide is easily reduced by carbon at a red heat. The purified tinstone, "black tin," contains about 65 to 70 per cent. Sn in place of 78·7 per cent. in pure SnO_2. It is mixed with about one-fifth of its weight of anthracite breeze, moistened to agglomerate it, and introduced into a reverberatory furnace. On account of the completeness with which the gangue has been removed, the use of a flux is not always necessary, but should the silica present be more than sufficient to combine with the oxide of iron, a little lime or fluor spar is added. After the temperature has been raised for six hours, the atmosphere being kept a reducing one meanwhile, the charge is raked, and more anthracite thrown in. The temperature is again raised, and the metal tapped off into an adjacent well lined with firebrick. Most of the slag flows out with the tin, and is mechanically removed from the well, the metal being ladled into ingots. The pasty slags which remain in the furnace retain a considerable proportion of tin globules, which are recovered by crushing and washing. The slags that flow out with the tin are again treated by liquation and smelted, and another fraction of tin recovered. The smeltiug of the slags is usually carried out in blast furnaces, a somewhat higher temperature being employed than in ordinary smelting. The tin obtained is somewhat impure, and is used for making common tin. The final slags consist mainly of ferrous silicate.

Although the use of reverberatory furnaces is more general, small blast furnaces are employed in several localities for smelting stream tin, especially in Saxony, the Malay Peninsula, and the islands of Banca and Billiton; the loss of tin by volatilisation

is very considerable. The furnaces are usually rectangular; the Saxon furnace is constructed mainly of granite, while the so-called "Chinese furnaces" in the Malay Peninsula are somewhat primitive constructions of rammed clay. The furnaces are kept full of the charge, which consists of ore, slag, and charcoal, and which is damped with water from time to time to keep the furnace from becoming too hot. The reduced tin is collected in wells in front of the furnaces, and is afterwards refined.

3. **Refining of the Tin.**—Crude tin contains Fe, Co, W, Cu, Pb, As, Sb, Bi, and S in varying amounts. In the refining of tin, advantage is taken of its low melting point, 232° C. = 450° F., by the use of a liquation process. The ingots are piled on the higher end of a sloping hearth and maintained at the melting point of tin. The less fusible metals—*e.g.*, Fe and Cu—together with As and S, remain on the hearth (still containing, however, about 20 per cent. of tin), and the bulk of the tin, together with the more fusible metals, such as Pb and Bi, is collected in a pot, where it is poled with green wood; during this process the agitation of the metal by the gases which escape from the wood aërates it sufficiently to oxidise the more readily oxidisable impurities. The metal is allowed to settle in the pot, when the remaining heavier impurities subside, the upper portion being ladled into ingots and marketed as refined tin, containing 99 to 99·5 per cent. Sn.

Grain tin is refined tin which has been heated to a temperature at which it becomes brittle and has been broken into fragments. The less pure grades of tin (**common tin**) are cast from the middle portion of the contents of the pot. The crude tin, whether that left on the liquating hearth or that separated at the bottom of the refining pot, is known as "hard head"; it contains about 60 per cent. Fe, 18 per cent. Sn, 20 per cent. As, and 2 per cent. S, and is re-worked for the tin it contains. An ingot of pure tin should be smooth and rounded, sharp edges and a frosted surface indicating the presence of impurity, and if this be very great the colour may be of a yellow or purple tint.

Promising attempts have been made recently to "Bessemerise" "hardhead." By blowing air through the molten material there is produced a highly ferruginous slag, fume rich in arsenic, and impure residual tin.

Recovery of Tin from Tin Plate Scrap.—Electrolytic methods of smelting tin ore or of refining the crude metal have no industrial existence. Methods have been proposed, however, for treating tin scrap, not only to recover the tin, but to leave the iron in a condition suitable for subsequent treatment in the open hearth furnace. One electrolytic method is that in which

the tin scrap is made the anode in a caustic soda solution, whereby the tin dissolves as stannate, and is subsequently deposited in the metallic state. The process is attended with numerous difficulties, however, owing to the rapidity with which the caustic soda becomes inactive through absorption of carbon dioxide, and to electro-chemical difficulties arising from the necessity of keeping the bath warm. More promising processes are those in which a solution of ferric chloride (*Browne and Neil process*) or stannic chloride (*Bergsoe process*) is used as a solvent for the tin. In the former a solution of ferrous and stannous chlorides is thus obtained, and is electrolysed in a series of vats, the outer cathode compartments of which are of concrete and the inner anode ones of porous earthenware. The cathodes are of pure sheet-tin, and the anodes of graphitised carbon. The chlorine liberated at the anodes oxidises the ferrous chloride to the ferric state, and thus regenerates the leaching agent, making the process cyclic in character. In the Bergsoe process the electrolyte is a solution of stannous chloride, and the leaching agent is similarly regenerated by oxidation of stannous to stannic chloride at the anodes. In both cases tin is deposited at the cathode in the form of large crystals. The *Goldschmidt chlorine process* is purely chemical. The tin scrap, absolutely free from moisture and all organic matter, is pressed into bundles, packed in baskets, and lowered into a large upright cylinder. Chlorine gas is forced in under pressure, and is rapidly absorbed by the tin with evolution of so much heat as to necessitate the cylinder being cooled. When absorption is complete the residual chlorine and stannic chloride are expelled in the gaseous state, and the bundle of scrap iron, after washing, is ready for treatment in the open hearth furnace. Where chlorine is available the process is to be preferred to the electrolytic methods.

4. **Uses of Tin.**—The metal is seldom used alone, save for tubes and linings coming into contact with mineral and aerated waters; it is used for this purpose on account of the circumstance that it is one of the metals which are not attacked by water.

Pure tin has a specific gravity of 7·29; its melting point, as already stated, is 232° C. It is brittle at ordinary temperatures, and is too weak as well as too costly (£160 to £180 per ton) for use as a structural material. It is malleable at 100° C. = 212° F., and becomes brittle again at 200° C. = 392° F. Its malleability allows of its extension to the form of foil. Much common "tin foil" is, however, made from lead coated on each side with tin and then beaten thin.

The chief application of tin is in the manufacture of tin plate (p. 32). The resistance of the metal to most vegetable and

animal juices, and the fact that when it is wiped on to a clean surface of copper it adheres as does solder, renders tin useful for lining cooking vessels. Its chief alloys are gun-metal and bronze (see *Copper*, p. 264), solder and pewter (see *Lead*, p. 284), and **Britannia metal**, which usually contains about 90 per cent. Sn, *8 per cent. Sb. and 1 to 2 per cent. Cu.* **Speculum metal** (for metallic mirrors) is a white, hard, brilliant alloy, of 2 parts of copper and 1 of tin, sometimes hardened by the addition of arsenic; the tin thus hardened will take a good polish and can be electro-plated. Tin-amalgam (from tin foil and mercury) is used for making mirrors, and is prepared from tin containing from 1 to 2 per cent. of copper which hardens it (p. 323).

Other alloys of tin are dealt with under copper and lead. Grain tin is made for the express purpose of producing "chloride of tin" (stannous chloride, used as a mordant), its finely-divided condition aiding its dissolution in hydrochloric acid.

When *tin is exposed to very low temperatures its crystals* become differentiated and the metal assumes a grey appearance (*grey tin*); its specific gravity in this condition is 5·7, but the metal reverts to its normal state when heated. The spontaneous disintegration of tin which has been observed in cold climates *may be accounted for by its conversion into the grey crystalline* variety. At ordinary temperatures common white tin is in a metastable condition, but the change to stable grey tin takes place with extreme slowness; the rate of change, however, is accelerated by lowering the temperature. This grey variety is the stable form of tin below 20° C.; between 20° and 170° C. the stable form of tin is tetragonal, while above 170° C. it is rhombic.

ANTIMONY.

Sources of Antimony.—This metal occurs native, to a trifling extent, in massive form, associated with gold, silver, and arsenic. It occurs as sulphide in **grey antimony ore** (*stibnite*). This is the most important ore of antimony, and consists essentially of the sulphide, Sb_2S_3. It resembles galena in colour, but has a lower specific gravity—viz., 4·7. It is found in Australia, Borneo, Japan, Germany, France, Italy, and Hungary. The pure sulphide contains 72·8 per cent. Sb; the ores actually worked may contain about 50 per cent. Thioantimonites of different metals also occur naturally—*e.g.*, *pyrargyrite*, $3Ag_2S \cdot Sb_2S_3$; *jamesonite*, $2PbS \cdot Sb_2S_3$.

Oxides of antimony form various minerals, such as **Senarmonite,**

Sb_2O_3, and **antimony ochre**, Sb_2O_4. **Red antimony** or **kermes mineral** is an oxysulphide, $Sb_2S_3 . Sb_2O_3$.

Winning of Antimony.—Antimony ores are usually rich enough to be worked directly, but a concentration process is practicable, and has been applied; this depends on the fusibility of antimony sulphide, which can be liquated from the gangue (see *Liquation of Tin*, p. 300). The liquation may be carried out in a reverberatory furnace, or in crucibles with an exit tube from the lower part, or in vertical retorts worked continuously. The liquated antimony sulphide is called "crude antimony," the metal itself being known as "regulus of antimony." As in the case of lead and copper, the sulphide and oxide of antimony will react with each other at a high temperature, with the production of free metal and SO_2. This is sometimes taken advantage of in the self-reduction process. For this purpose the antimony is roasted until part of it is oxidised to Sb_2O_4, which is then heated in crucibles with raw ore, the following reaction occurring:—

$$3Sb_2O_4 + 2Sb_2S_3 = 10Sb + 6SO_2.$$

It is usual to cover the contents of the pot with a mixture of charcoal and sodium carbonate (or with tartar as an equivalent). It is probable that the reduction may be partly due to the removal of the sulphur by the alkaline carbonate.

The reduction of antimony is more usually effected by the use of iron, as in the so-called "precipitation" process for smelting galena (p. 273). Any considerable excess of iron is avoided, as it is soluble in metallic antimony.

The ground ore is mixed with about one-third of its weight of wrought-iron scrap (tin-plate cuttings), one-tenth of its weight of salt, and some slag from a previous fusion; the mixture is charged into fireclay crucibles, holding about ½ cwt. apiece. The actual amount of iron required is determined by analysis, and a slight excess is used. A ball of scrap tin plate is put into the mouth of the crucible, a trace of tin in the antimony whitening the metal and improving its crystalline appearance (*v.i.*). Forty such crucibles are introduced through the holes in the roof of a long furnace having a hearth at each end. As the charge melts, the ball of scrap tin is pushed down, and in about three hours the reduction is complete. The main reaction is represented by the following equation:—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The contents of the crucible is then poured into an iron mould, and when it has set the slag is knocked off from the metal collected at the bottom. This metal is known as "singles," and contains

about 91·5 per cent. Sb, 7 per cent. Fe, and 1 per cent. S. It is broken up and submitted to the process of "doubling," for which about 80 lbs. is charged into a crucible, together with 7 or 8 lbs. of liquated sulphide of antimony and 4 lbs. of salt, which may with advantage be kelp-salt.* The antimony sulphide is added in order to convert the iron of the crude antimony into sulphide, a corresponding quantity of antimony being obtained as metal. The fused mass is skimmed and the metal cast.

This metal contains 99·5 per cent. Sb, 0·2 per cent. Fe, 0·2 per cent. S, and is known as "starbowls."

The process of refining antimony is known as "starring," because the finished metal has a stellate crystalline appearance. It is carried out by freeing the metal obtained in the "doubling" process from slag, and charging about 80 lbs. of it into the crucibles nearest the fire of the same furnace as is used for the preceding operations, together with 8 lbs. of "antimony flux," which consists of crude potash melted with liquated antimony sulphide. This flux removes the remaining Fe and S; the efficiency is to be ascribed to the ease with which thioantimonites and thioantimonates are formed, the alkali sulphide uniting with antimony sulphide to produce these substances. Care is taken not to saturate the flux, during its preparation, with antimony sulphide, so that it may take up its quota from the metal. It is revivified occasionally by the addition of a little potash. The purified metal is cast into ingots, and is known as "star antimony."

Much fume is produced in the smelting of antimony, and is condensed in flues. It consists mainly of oxides of antimony, and contains about 70 per cent. Sb, which amounts to about 10 per cent. of the antimony in the ore treated. It is mixed with coke, and worked up with the ore in melting for "singles."

A short process has been introduced, with satisfactory results, at Mayenne, France, involving only two steps:—Fusion with scrap iron to produce crude metal, followed by a refining fusion. The process is carried out in reverberatory furnaces, and consists in dropping the heated antimony ore into a fused bath of iron sulphide and iron at a high temperature, whereby it is rapidly decomposed. Separated antimony sinks to the bottom, some slag is skimmed from the top, and more iron is added. When all the antimony is reduced it is tapped out, the slag and a portion of the iron sulphide removed, and the remaining iron sulphide

* *Kelp-salt* is obtained in the manufacture of iodine from kelp, and contains some 10 per cent. of sodium carbonate, the balance being chiefly common salt.

heated up ready for the next charge. The impure antimony is refined by fusion with soda in a similar furnace.

Antimony is occasionally won by roasting to oxide and reduction with carbon. The process is tedious, and involves five stages.—(1) Liquation; (2) oxidation by roasting; the temperature of roasting must be kept low, as the sulphide is very fusible: (3) reduction of the oxide with coal in reverberatory or blast furnaces to yield crude metal; (4) refining by fusion with soda: and (5) treatment of volatile oxide caught escaping from the oxidation roast. In modern practice the ore is sometimes smelted in a water-jacketed furnace to produce a matte containing a little iron; this matte is then treated in a small converter to produce antimony oxide, which is subsequently reduced with coal. Antimonial lead is now sometimes produced designedly by smelting jamesonite (*q.v.*) or a mixture of stibnite and galena free from silver in the blast furnace. The product sells for its full alloy value.

French Volatilisation Process.—In recent years there has been remarkable progress in the metallurgy of antimony. The older process of liquating stibnite ore and precipitating the antimony by iron is fast disappearing. The economical treatment of auriferous and argentiferous ores was formerly a perplexing problem, but it has been solved by the simple volatilisation process, introduced and practised in France, and with which the names of Chatillon and Herrenschmidt are closely connected. The more modern method is to charge the ore with fuel in a small shaft furnace, and urge the fire with a large excess of air. The antimony sulphide liquates out, is oxidised, and the oxide (Sb_2O_3) is condensed in suitable chambers and flues in connection with the furnace. The purity of the condensed oxide varies greatly in the different chambers of the condensers, though it is not uncommon to obtain a product carrying 98 to 99 per cent. of oxide. Arsenic oxide is the chief impurity. For reduction to metal this oxide is briquetted and charged into a reverberatory furnace with coke and sodium carbonate in the proportion of 70 oxide, 7 soda, and 8 carbon. The process is applicable to all kinds of ore. The shaft furnace is designed on the lines of a gas producer lined with aluminous brick, and with a bottom of movable grate bars permitting the tapping of the partly fused slag. As soon as the charged ore meets the column in the furnace volatilisation commences, and by the time the slag is raked from the bottom bars the antimony has been entirely driven out, while all the precious metals are retained. The excess heat of the shaft furnace is used to reduce the antimony oxide in a contiguous open hearth furnace, which is lined with chrome brick. The

waste heat from the latter is used for power purposes. The various processes, such as the Chatillon and the Herrenschmidt, differ mainly as regards the arrangements for condensing the oxide. These include chambers, cast-iron flues, and tanks, often water-cooled, and cotton bags, such as are used in lead and zinc smelteries.

A. Germot proposes to treat molten antimony sulphide by injection of air in a converter. The oxygen burns part of the sulphur in the ore, producing SO_2 and antimony, which remains in the crucible. The operation becomes continuous by the addition of further quantities of ore. The SO_2 escapes at the top of the converter, and carries with it antimony sulphide fumes, which are condensed in special compartments. If, instead of working in closed vessels, a current of air is brought to act in these fumes, antimony oxide or oxysulphides are produced according to the proportion of air. The products are said to be suitable for use in the arts, or for subsequent treatment to produce antimony.

Electrolytic Winning of Antimony.—Antimony has been produced commercially in the form of plates about 2 mm. thick by the Siemens and Halske electrolytic process. The antimony sulphide in the ore is leached out with a solution of sodium-sulphide. The solution is passed through the cathode compartments of a series of cells, and the antimony deposited on iron cathodes. The anode compartments, separated from the cathode compartments by porous diaphragms, contain a solution of common salt, in which are carbon anodes; chlorine is given off at these, and is utilised for the manufacture of bleaching powder or chlorate. The solution passing from the cathode compartments consists chiefly of sodium sulphide, containing little or no antimony, and is used to leach a fresh portion of ore. The porous diaphragm prevents the oxidation of the sodium sulphide by chlorine. Other methods have been suggested, but not used on a commercial scale.

Properties and Uses of Antimony.—Antimony is a greyish-white, hard, crystalline metal, of specific gravity 6·7; it melts at 630° C. = 1,166° F. Unstable yellow and black modifications also exist. The yellow form is obtained by the action of oxygen on liquid stibine, SbH_3, at − 90° C., and by the action of chlorine on stibine, both dissolved in liquid ethane (C_2H_6) at − 100° C. It is amorphous, and above − 90° C. readily passes into the black variety. The latter can also be prepared by the rapid cooling of antimony vapour, and by the action of oxygen on stibine at − 40° C. It is an amorphous powder with specific gravity 5·3, and when heated passes into the stable metallic variety. Antimony is but little used alone. When precipitated from solution

by zinc it is obtained as a fine black powder, which is employed for the purpose of imparting to plaster casts the appearance of iron or steel: the powder is known as "antimony black" and "iron black." The metal serves as a basis for the manufacture of salts used in the arts and in medicine (*e.g.*, tartar emetic), and of its oxysulphide (antimony vermilion), which is used as a pigment (see Vol. II.). Its chief use is in hardening other metals, notably lead and tin, for type metal, Britannia metal, pewter, etc. These alloys, including antifriction metals, are considered under lead and tin.

BISMUTH.

This metal occurs **native** to a considerable extent, native bismuth being indeed its chief source. It is found in masses and in veins; small deposits occur in Cornwall and Cumberland, but Bolivia, Germany, and Australia supply the largest quantities. Crude native bismuth contains 7 to 12 per cent. of the metal, the remainder being gangue. The following ores of bismuth are found in limited quantities:—Oxide (**bismuth ochre**), carbonate (**bismuthite**), sulphide (**bismuth glance**), and **copper bismuth glance** ($3Cu_2S + Bi_2S_3$). These ores are rarely found alone, being usually associated with other minerals.

Winning of Bismuth.—Formerly bismuth was obtained by simply heating the ore in sloping iron tubes, the liquated metal being collected in pots. The method was a wasteful one, and has now been entirely abandoned. A smelting method is now always employed. The chief difficulty that presents itself in the metallurgy of bismuth is the great volatility of the metal. This precludes the employment of the blast furnace for the reduction process, necessitates great care in calcining the ore, and renders necessary the use of expensive fluxes to form slags which fuse at a low temperature. The application of wet methods of extraction is restricted by the difficulty of dissolving bismuth and its compounds.

The ore is first submitted to a concentration process. This is somewhat difficult, owing to the brittleness of the minerals. An efficient system of hand-picking is usually adopted, while magnetic separation has also been successfully applied when the gangue is of a suitable nature. The ore is then crushed to an appropriate size and roasted. Bismuth minerals do not lend themselves to roasting in heaps and kilns, and for this purpose long hearths or multiple hearth reverberatory furnaces are used. Constant rabbling is necessary to keep the mass from agglomerating, while arsenic and antimony must be eliminated by reducing

arseniates and antimonates in the usual manner—*i.e.*, by adding small quantities of crushed coke. It is also advantageous to dampen the fuel, as the presence of steam greatly facilitates the elimination of arsenic and antimony by reacting with their sulphides, thus :—

$$As_2S_3 + 3H_2O = As_2O_3 = 3H_2S.$$

Oxidised ores, of course, may be smelted direct without roasting. The smelting process is carried out in crucibles or reverberatory furnaces, the former being employed only when small quantities of ore are handled. Any small reverberatory furnace may be adapted to the treatment of bismuth ores. Owing to the penetrating nature of the molten metal, however, it is advisable to employ a furnace specially designed for the purpose, in which the bed consists of successive layers of sand fritted together and saturated with slag. The charge consists of a mixture of ore, soda, oxide of iron, lime, old slags, from 3 to 5 per cent. of crushed coke, and sometimes a little fluor spar. The mass boils during reduction, and when the reaction is over the temperature is raised rapidly, and the molten material run into moulds in which the different constituents separate. The products of this operation are generally crude bismuth, matte containing most of the copper, speiss containing arsenic, nickel, and cobalt, and slag. A precipitation process of smelting similar to that used for lead was formerly employed, but has now been abandoned.

A wet method of obtaining bismuth from oxidised ores, such as bismuth ochre and bismuthite, consists in dissolving the material in hydrochloric acid to saturation, and precipitating the metal by metallic iron. The black sludge thus produced is washed and fused in a crucible. When argentiferous lead contains bismuth, the last part of the cupellation slag contains the bismuth, which is less easily oxidisable than lead. This "black litharge" is extracted with hot hydrochloric acid, leaving insoluble chloride of lead (and of silver if present), and the solution is precipitated by the addition of much water, a bismuth oxychloride being thus obtained, which is reduced by fusion with charcoal and an alkaline flux.

The Refining of Bismuth.—Saxony bismuth may contain over 99 per cent. of bismuth, frequently as much as 99·7 per cent., the chief impurities being As, Cu, and Ag. Cruder samples, from Peru and Australia, containing 93 and 94 per cent. Bi, 3 to 4 per cent. Sb, and some 2 per cent. of Cu, may be purified by liquation on an inclined iron plate.

The method adopted to purify the metal is exactly similar to

that employed in softening and refining lead (*q.v.*)—namely, *exposure of the molten bismuth to the oxidising influence of the* atmosphere. The impurities have a greater affinity for oxygen than bismuth, and are removed from the surface as dross. A method sometimes employed consists in melting the crust metal in iron kettles under a layer of NaCl, KCl, NaOH, and sufficient bismuth oxychloride (BiOCl) to convert the lead to $PbCl_2$, a corresponding amount of bismuth being set free. Antimony is removed in the same way with a flux of soda, potash, and sulphur, sodium sulphantimonate being formed, whilst for arsenic the flux used is caustic soda and nitre.

When specially pure bismuth—*e.g.*, for medicinal purposes—is needed, modes of purification specially adapted for each impurity to be eliminated are employed. Thus, according to Matthey, arsenic may be removed by stirring the fused metal, kept at a temperature of 395° C. = 743° F. in contact with air, the whole of the arsenic being eliminated by volatilisation as oxide at 513° C. = 955° F. Antimony rises to the surface of fused bismuth as a film rich in antimony which can be skimmed off, the temperature most suitable for the operation being 350° C. = 662° F. The antimony oxidises during this process, and forms a glass consisting largely of oxides of antimony. Copper can be got rid of by fusing the metal and stirring in sodium sulphide, a slag containing copper and some bismuth being formed. The skimmings contain, on an average, about 10 per cent. of the bismuth treated, and are re-worked. For the removal of gold and silver about 2 per cent. of zinc is added to the fused metal, as in the Parkes process for desilverising lead (p. 280). The skimmings are fused with borax for the recovery of the precious metals. Argentiferous bismuth may also be refined by pattinsonising (p. 278). When a metal approximately chemically pure is required, a wet process is probably most suitable, the bismuth being obtained as a basic salt which is reduced with pure reducing agents and fluxes. Bismuth containing 99·9 per cent. Bi can be thus obtained.

Properties and Uses of Bismuth.—*Bismuth is a greyish-white* metal of specific gravity 9·8, characterised by the ease with which it crystallises (in cubes often arranged in hollow pyramids, like NaCl). It melts at 268° C. = 514° F., and expands considerably on solidifying.

Bismuth, lead, tin, and cadmium form simple alloys with each other—*i.e.*, their mixtures consist of pure metals and eutectics. These alloys melt below the boiling point of water, and are known as "fusible metals," and are used largely for stereotyping.

	Wood's Metal.	Lipowitz Metal.	Rose's Metal.
Bismuth, ...	4	15	2
Lead, ...	2	8	1
Tin, ...	1	4	1
Cadmium, ...	1	3	0
Melting point, . . .	60·5° C.	60° C.	94° C.

Their melting point can be still further reduced by the addition of mercury. Bismuth is also used in the manufacture of a soft solder, used in soldering pewter, while alloys with lead, tin, and antimony are made which fuse at some particular temperature above 100° C., and serve as safety plugs for boilers and automatic sprinklers. In conjunction with antimony, bismuth is used for making thermo-electric couples. Bismuth salts are largely used for medicinal purposes; the oxychloride is used in face powders, and the nitrate for cosmetics. The oxide is used to a small extent in making porcelain colours, and in the manufacture of glass for optical purposes.

NICKEL.

The most important ore of nickel is a mineral consisting of magnetic iron pyrites (Fe_3S_4—pyrrhotite), containing nickel in place of iron to the extent of about 3 to 8 per cent.; this is associated with chalcopyrite (copper pyrites, $Cu_2S . Fe_2S_3$). This nickel ore is free from arsenic, and contains a trace of cobalt and platinum.* It is found at Sudbury in Canada deposited in diorite, a rock composed of hornblende and triclinic felspar.

Garnierite.—This is an hydrated silicate of nickel and magnesium, found in New Caledonia and the Ural Mountains, of a composition corresponding approximately with the formula $NiMg(SiO_3)_2 3H_2O$. The proportion of nickel to magnesia is, however, not strictly in accordance with this formula, and the ore is commonly associated with oxides of iron and siliceous gangue. The percentage of nickel ranges from 1 to 35 per cent., averaging about 10 per cent. Another ore, also found in New Caledonia, but of less importance than garnierite, contains cobalt and manganese in addition to nickel. Garnierite is remarkable for being almost the only nickel ore which is practically free from cobalt.

* As sperrylite, see p. 345.

Arsenides, antimonides, and **sulphides** of nickel have been longer known as sources of the metal than have the two foregoing ores. These constitute the European ores, and occur principally in Saxony, Bohemia, and Scandinavia. *Kupfer-nickel* (NiAs), specific gravity 7·4, *antimonial nickel* (NiSb), *nickel glance* ($Ni(AsS)_2$), *nickel blende* (NiS), and *nickeliferous iron pyrites* are examples of this class of ore.

Winning of Nickel.—Nickel, standing metallurgically between iron and copper, can be won by processes analogous with those proper to both the latter metals. Thus, sulphide ores may be run to a matte (although this cannot be self-reduced), and oxide ores directly reduced to crude metal. A similar relation is evident in the behaviour of nickel when treated by the wet methods of extraction, which resemble those for copper, although this process will not serve for the direct precipitation of nickel as metal, its similarity to iron preventing such easy reduction. The stability and volatility of nickel chloride ($NiCl_2$) and the existence of nickel carbonyl, $Ni(CO)_4$, have led to suggestions for winning nickel directly by the volatilisation of the metal from the ore in the form of these compounds. At the present time nickel is mostly obtained from garnierite and nickeliferous pyrrhotite and chalcopyrite. European ores are now very little worked.

Extraction of Nickel from the Sudbury Ores.—As examples of these ores the following analyses may be quoted :—

	1. Per cent.	2. Per cent.
Silica,	13·44	24·55
Iron,	39·02	35·18
Sulphur,	26·26	18·27
Copper,	4·31	1·43
Nickel,	5·57	3·74
Alumina,	4·49	8·02
Lime,	2·28	2·06

About 0·1 per cent. of cobalt occurs in these ores.

The ores are crushed and hand-picked into copper ore and nickel ore; the latter is roasted in heaps for several weeks until the sulphur is reduced to about 7 per cent. and the bulk of the iron oxidised. The ore is next put through a water-jacketed cupola in which the siliceous gangue is fluxed by the oxide of iron, alumina and lime, and the sulphides of copper, nickel, and iron run down to a matte of the following composition :—

	Per cent.
Copper,	20 to 25
Nickel,	18 to 23
Iron,	25 to 35
Sulphur,	20 to 30

The fused matte is tapped into a pot and the slag separated. The matte is next refined in a Bessemer converter similar to those used for copper mattes (see *Copper*, p. 248). During this part of the process the iron is oxidised * and fluxed, and a matte corresponding with "fine metal" (see *Copper*, p. 245) obtained, having the composition Cu 45, Ni 40, S 5 to 15 per cent. Owing to the fact that nickel sulphide stands between iron sulphide and copper sulphide in respect of the ease with which it is oxidised, care has to be taken in stopping the blow at the point when the iron is completely oxidised. As there is no definite indication when this point is reached, the success of the operation depends wholly on the judgment of the workman.

The Bessemer matte serves for the production of Ni and Cu alloys—*e.g.*, German silver—for which purpose the sulphur is removed by roasting and the substituted oxygen by reduction with charcoal, or other carbonaceous matter. The resulting alloy, consisting of 50 per cent. Cu and 49 per cent. Ni, is very similar to nickel in appearance, but has a lower melting point.

For the separation of nickel from the Bessemer matte two processes are in use—viz., the *Orford process*, also known as the "tops and bottoms" process, and the *Mond process*. In the former the matte is mixed with coke and salt cake (crude sodium sulphate)—50 tons of matte, 30 tons salt cake, and 7 tons coke—and smelted in a blast furnace or a magnesia-lined open hearth reverberatory furnace. The fused mass is tapped out and allowed to separate into two layers. The top layer ("tops") consists of a solution of copper and iron sulphides in sodium sulphide, the latter being formed by the reduction of salt cake. The bottom layer ("bottoms") consists essentially of nickel sulphide, with small quantities of iron and copper: it may need resmelting into tops and bottoms. The nickel sulphide is then roasted "dead" with the addition of a little nitre and salt. The latter converts any copper into chloride which is afterwards leached out. The residual nickel oxide is reduced to metal as described later. The "tops" is treated for the recovery of copper and sodium sulphide. **The Mond process** depends on the formation and decomposition of the volatile nickel carbonyl, $Ni(CO)_4$. The Bessemer matte is crushed and roasted in mechanical furnaces. The finely-crushed roasted material is then leached with dilute sulphuric acid, which removes the greater part of the copper (about two-thirds). The dried residue, consisting of oxides of nickel, copper, and iron is then exposed to the reducing action of water gas ($CO + H_2$) at a temperature of 300° to 400° C. in

* The greater ease with which iron is oxidised and converted into silicate than is nickel, is utilised in this and similar separations.

a tower containing a series of shelves, the roasted material being made to fall from one shelf to another by means of rabbles. The reduced nickel, which also contains metallic copper, and probably some oxide of iron, is then passed by air-tight conveyors to the "volatiliser," which is very similar to the reducing tower, and converted into the gaseous carbonyl by exposure to carbon monoxide at a temperature of about 50° C. The carbon monoxide is prepared by passing the gas from the "reducer" over red-hot carbon. The gaseous product is then carried forward into the "decomposer," a cylindrical vessel containing nickel granules, where it is exposed to a temperature of 200° C. In this way nickel is deposited on the granules, which are kept in motion by the constant withdrawal of some of them from the bottom of the vessel by means of a worm conveyer. The gas from the "volatiliser" is filtered free from dust before passing to the "decomposer," and after decomposition the carbon monoxide is again used for extracting more nickel. The residue in the "volatiliser" must be returned to the reducer, and thus kept in circulation for several days before extraction of nickel is complete.

Extraction of Nickel from New Caledonian Ore (Garnierite).—As the ore is a double silicate of nickel and magnesium, free from sulphur, an obvious method of treating it consists in reducing it with carbon, using limestone as a flux, in a blast furnace, thus obtaining a crude metal corresponding with cast iron. The composition of the "fonte" obtained in this manner is given below:—

	Per cent.
Nickel,	70·70
Iron,	22·00
Graphite,	1·78
Sulphur,	1·65
Aluminium,	1·37
Magnesium,	0·10
Oxygen and combined carbon,	1·88

The crude metal may then be converted into a sulphide matte in a manner similar to that about to be described.

This process, though simple in principle, has proved unsatisfactory in practice owing to the refractory character of the nickel and its slags, which are rich in magnesia. An improvement consists in winning the nickel as a sulphide matte by running down the ore with half its weight of gypsum or alkali waste and 20 per cent. of coke. The nickel is thus converted into sulphide and a portion of the iron fluxed as silicate. The resulting matte contains 50 to 55 per cent. Ni, 20 to 30 per cent. Fe, and 16 to 18 per cent. S. It is refined either in a Bessemer converter, or

by roasting and fusion with sand to flux the iron as silicate, the nickel being obtained as sulphide. This is crushed, roasted to oxide, and reduced to metal in the manner described below. The ore is, however, now generally imported into Europe and worked by wet methods—*e.g.*, by dissolution in hydrochloric acid and precipitation of the nickel as oxide.

Extraction of Nickel from European Ores (Arsenides, Antimonides, and Sulphides).—The pyritic ores, containing some 2 per cent. Ni, 50 per cent. Fe, and 30 per cent. S, are roasted in heaps and fused for a coarse metal. In these processes iron is oxidised and fluxes the siliceous gangue. The resulting coarse metal contains about 5 per cent. Ni, 2 to 5 per cent. Cu, 30 per cent. S, and 60 per cent. Fe. It is roasted in heaps and smelted in small blast furnaces with quartz, to flux the oxide of iron produced by the roasting.

The amount of nickel in this regulus is about 50 per cent. and the copper 25 per cent., the remainder being iron and sulphur. A fusion for a fine metal in an oxidising furnace then follows, the remainder of the iron being thus oxidised and fluxed by added quartz. The fine metal contains 60 per cent. Ni, 30 per cent. Cu, 8 per cent. S, and 0·5 per cent. Fe. (In processes of this type, especially as formerly practised, the main product was an alloy of Ni and Cu, the demand for nickel itself being but small). In order to completely desulphurise the fine metal, it is ground and roasted "dead," the mixed oxides being subsequently reduced in crucibles with powdered charcoal. To obtain pure nickel from the roasted fine metal, advantage may be taken of the greater solubility of copper oxide than of nickel oxide in dilute sulphuric acid, the residue of nickel oxide left by this treatment being subsequently reduced (*v.i.*).

Arsenical nickel ores are worked to a speiss either in working argentiferous lead ores (see *Lead*, p. 277) or, occasionally, as a separate process, consisting of roasting in heaps and smelting with quartz in a blast furnace. The coarse speiss contains about Ni 45 per cent., Co 4 per cent., Cu 0·75 per cent., Fe 10 per cent., S 4 per cent., As 36 per cent. By melting this in a reverberatory furnace with a siliceous slag, the iron is fluxed and much arsenic oxidised and volatilised. The fluxing is continued until the blue tint of the slag indicates that the scorification of cobalt is beginning. The roasting is continued so long as it is possible to remove solidified oxides from the surface of the bath. The refined speiss contains 60 per cent. Ni, 3 per cent. Co, 1 per cent. Cu, and 36 per cent. As. It is ground to powder and roasted until it has acquired a bright green colour, being converted into nickel arsenate, $2NiO . As_2O_5$. By heating this to a very high

temperature in a reducing atmosphere, the arsenic is volatilised and a portion of the nickel reduced to metal. This material still contains 1 to 2 per cent. As, which is removed by fusion with sodium nitrate and carbonate and subsequent washing with water, being thus dissolved as sodium arsenate. The nickel oxide is then reduced.

Much speiss is imported to Birmingham, where it is fused with lime and fluor spar, ground and roasted to free it from most of the arsenic. The subsequent treatment is designed for the recovery of the cobalt; the roasted speiss is dissolved in hydrochloric acid, the iron in the solution peroxidised by bleaching powder, and chalk is added; this precipitates both iron as basic carbonate and arsenic as ferric arsenate. The copper is thrown out by H_2S, the solution again peroxidised by bleaching powder, and lime added to neutralise the hydrochloric acid liberated by the precipitation of the copper. Cobalt peroxide is thus thrown down, it being more readily formed than the corresponding nickel compound. The nickel still in solution is precipitated as the normal oxide by milk of lime.

In the **reduction of nickel oxide,** obtained in any of the above processes, it is not generally economical to fuse the resulting metal, as its meltiug point is high (about 1,430° C.). It is, therefore, usual to make the oxide into a paste with charcoal and carbonaceous material, such as flour or oil, and compress it into slabs which are cut into small cubes, the shape of which is retained by the metal when reduced. With modern regenerative furnaces, however, nickel can be completely fused and obtained as cast metal. Commercial nickel is never pure, but contains, like iron, carbon and silicon. The following are analyses of cast nickel :—

	I. Per cent.	II. Per cent.
Carbon,	1·10	...
Silicon,	0·13	0·19
Iron,	0·10	0·30
Sulphur,	0·26	0·07
Nickel,	98·39	98·68
Copper,	...	0·76

Electrolytic Processes: Refining Nickel.—The electrolytic winning of nickel from its ores has not yet been accomplished. Within the last few years, however, the refining of nickel has been practised in this country and in America. A good deal of secrecy has been maintained regarding the details of these processes, but it may be taken that they are substantially as follows: —The anodes are of copper-nickel alloy, obtained by roasting and reducing Bessemer matte as mentioned above. Cast cakes of the matte itself have also been used with more or less success.

The cathodes are of thin sheet-copper, and the electrolyte is an acid solution of the mixed sulphates or chlorides of copper and nickel, made by dissolving the matte or alloy in some suitable agent. The solution is heated and kept in circulation, and during electrolysis copper is deposited, while nickel and a little iron remain in solution. Arrangements are made for maintaining the strength of the electrolyte. When sufficiently rich in nickel the latter is withdrawn, and the remaining copper and iron precipitated by suitable means. The nickel solution is then made ammoniacal, and electrolysed, while hot, between anodes of lead or carbon and cathodes of sheet nickel. The strength of the electrolyte is maintained between certain limits, and the ammonia recovered by boiling. Electrolytic nickel persistently retains iron; its composition may be judged from the following analysis—

Ni,	99·20
Cu,	0·14
Fe,	0·58
S,	0·03
	99·95

The Orford Copper Company are reported to be using a process in which the anodes are of crude nickel sulphide obtained in the "tops and bottoms" process, a solution of nickel chloride serving as the electrolyte. Their method of dealing with the liberated sulphur is not known.

Successful experiments have been made at Sault Sainte Marie, in which ferro-nickel is produced by the electro-thermal smelting of Canadian nickel ores in the Héroult furnace (*q.v.*), and it is stated that the method is capable of commercial application.

Properties and Uses of Nickel.—Nickel has a specific gravity of 8·8; fuses at about 1,430° C., and ranks below iron in electrical conductivity. Nickel greatly resembles iron, differing from it mainly in its stability in air and water. It stands next to manganese in hardness, it is magnetic at ordinary temperatnres, but not at temperatures above 250° C. = 482° F. Cast nickel is not very malleable, owing to the presence of dissolved oxide, but may be improved in this respect by fusion with a powerful reducing metal—*e.g.*, magnesium, aluminium, or manganese—their action recalling that of phosphorus upon over-refined copper, p. 252. The metal can be readily welded. Nickel is principally used for alloying with copper to produce nearly white alloys of the German silver class, its whitening effect being remarkable.*

* An alloy containing about 66 per cent. Ni and 33 per cent. Cu, which greatly resembles nickel in appearance, is sometimes ignorantly or wittingly offered in its place. It may be detected by the fact that it is not attracted by a magnet.

It is probable that a compound of these two metals exists corresponding with the formula CuNi. The alloys generally used contain less than 25 per cent. nickel. **Coinage nickel** consists of Cu 75 per cent. and Ni 25 per cent., and is white in spite of the large proportion of copper. This alloy has also been used for locomotive firebox plates. Copper containing 5 per cent. Ni is used for the driving bands of projectiles, and with 3 per cent. Ni for locomotive boiler tubes. **German silver** varies much in composition, its value increasing with the proportion of nickel. It may be regarded as a nickeliferous brass, and ranges between the limits Cu 40 to 70, Zn 15 to 35, Ni 6 to 30 per cent. The impurities commonly present are lead, iron, and tin, and their effect is much the same as on brass (*q.v.*). These alloys consist of single homogeneous solid solutions, and as such possess a high electrical resistance. Among the special alloys which are used for electrical resistance may be mentioned :—

Constantan, .	60 % Cu, 40% Ni.
Platinoid, . .	60 % Cu, 14% Ni, 24% Zn, and 1·2% tungsten.
Nickelin, . .	74·5% Cu, 25% Ni, 0·5% Fe.
Manganin, . .	84 % Cu, 12% Ni, 4% Mn.

Nickel is largely used for the manufacture of nickel steel (see pp. 28, 221), in which the amount of nickel varies from 1 to 25 per cent., according to the use to which the steel is to be put. Guillaume has found that the addition of nickel to iron causes a decrease in the coefficient of expansion of the metal until the proportion of 35 per cent. nickel is reached, after which the coefficient rapidly increases. It is thus possible to prepare alloys possessing any desired coefficient of expansion. Guillaume's "**Platinite**" containing 46 per cent. Ni and 0·15 per cent. of carbon has the same coefficient of expansion as glass, and has entirely replaced platinum in the manufacture of incandescent lamps. Another ferro-alloy, "**Invar,**" containing 36 per cent. Ni, and 0·2 per cent. C is practically non-expansible by heat. The resistance of nickel to rust has led to its use for plating of other metals by electro-deposition. Its resistance to fused alkalies renders it applicable for laboratory vessels. A new alloy of copper and nickel, containing 70 per cent. Cu and 30 per cent. Ni., "**Monel metal,**" is now coming into commercial use for a variety of purposes (see p. 28). It is made direct from Sudbury ore.

COBALT.

This metal so nearly resembles nickel that the metallurgy of the two may be conveniently taken together. It is mostly a

bye-product in nickel works, being separated as already described after the removal of the remaining constituents of the ore. Definite cobalt ores are **smaltine** or **speiss cobalt (tin white cobalt),** $CoAs_2$, **cobalt glance,** CoAsS, **cobalt bloom,** $Co_3As_2O_8$ *(the normal arsenate)*, **black earthy cobalt,** *consisting of hydrated oxides of cobalt and manganese and* **cobalt pyrites.** *The metal itself is* more strongly magnetic than nickel; it has a specific gravity of 8·9, and a melting point of about 1,460° C. In the metallic state it is chiefly used for plating, yielding a better coating than nickel. Its main use, however, is in the production of pigments (*q.v.*, Vol. II.), for which purpose the peroxide separated in the systematic extraction of nickel already described is worked up. Cobalt ores are worked on the same general lines as those of nickel, but a process depending on the stability of cobalt chloride has also been utilised. The arsenides and sulphides are roasted, ground, mixed with ferric chloride, made into a paste with ferrous chloride, moulded, dried, and calcined. A chlorinating reaction typified by the following equation occurs:—

$$CoO + FeCl_2 = CoCl_2 + FeO.$$

The cobalt chloride is leached out and worked up by the wet method described above for the separation of nickel and cobalt.

MERCURY.

Mercury is found **native,** both alone and as an amalgam with silver. Native mercury may occur collected in cavities, or in a finely-divided state distributed through cinnabar. Its chief source, however, is its sulphide (HgS), found in the form of **cinnabar,** which is won in large quantities in Spain, Austria, South Russia, South China, and California. This is a heavy crystalline mineral (specific gravity 8·2), red or brown in colour. It is sometimes found in a black amorphous form (*metacinnabar*), the two varieties corresponding with the red and black form of HgS prepared in the wet way.

Methods of Winning Mercury from Cinnabar.—Owing to the ease with which mercuric oxide is decomposed, mere roasting of cinnabar yields SO_2 and Hg, not HgO. The removal of sulphur may be affected by other reagents than oxygen—*e.g.*, lime and iron. Two types of process for winning mercury from cinnabar may, therefore, be distinguished.

1. **Removal of the Sulphur by Roasting in Air.**—The crudest method of effecting this consists in roasting the ore in heaps, enclosed by brickwork, and provided with flues similar to those

sometimes used for coking coal (see *Coke*, Vol. II.). The mercury volatilised from the lower portion of the heap is condensed in the upper layer from which it may be washed on a sieve, the ore-dust and mercury being washed through, whilst the coarser portion is used for the lower layer of the heap next to be roasted. The process is adapted for treatment of copper ores (*fahlerz*) which contain from 0·5 to 17 per cent. Hg, and are afterwards to be worked for copper. In better processes the roasting is carried out in an enclosed furnace, and the mercury vapour condensed from the flue gases by passage through a series of receivers or chambers. Thus at Idria, by the old process, chambers like those shown in Fig. 47 serve for the condensation of the vapour expelled from the ore (containing 10 to 12 per cent. Hg), which is roasted on the shelves, *a*, *b*, *c*, disposed over the grate, A. The final chambers, D, are provided with water cascades to complete the condensation. The mercury collects in an underground channel. In the more modern Idrian furnace a

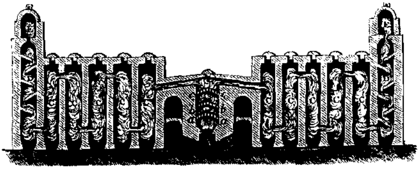


Fig. 47.—Old mercury furnace at Idria.

a, *b*, *c*, Shelves; A, grate; C, condensing chambers; D, water chambers; E, aperture for escape of gases.

continuous distillation is effected in a cylindrical kiln charged at the top through a hopper, and connected with six condensing chambers externally cooled by water. The spent ore is raked out through bars at the bottom of the furnace, and fresh charges introduced by the hopper. When once started, the reaction $HgS + O_2 = Hg + SO_2$ continues, as it is exothermic, but the heating effect is supplemented by the combustion of about 4 per cent. of charcoal added to the ore charged. For poor ores, which contain so much gangue that the combustion of their mercuric sulphide is insufficient to maintain the temperature of reaction, heating from some source other than the combustion of the ore is requisite. The direct admixture of fuel is not advisable, as sufficient oxygen for the combustion both of it and of the HgS

would be difficult to supply, and HgS would be sublimed unchanged. This necessitates the use of a reverberatory furnace, by which means an ample supply of air, together with the requisite heat, can be obtained. The plant for winning mercury from poor ores (1 per cent. Hg) by this method includes, therefore, a reverberatory furnace connected with a condensing chamber, which is coupled in its turn with a second chamber by means of a wide iron pipe, cooled by an external water spray. The necessity for the use of air as an oxidising agent causes the mercury vapour to be diluted with much nitrogen as well as SO_2, and, therefore, to be difficult to condense. When working poor ores, the dilution is increased by the gases of the external furnace, thereby making the use of the comparatively elaborate condensing arrangements described above inevitable. In any case, considerable loss of mercury must occur, as at the temperature of the exit gases mercury possesses an appreciable vapour tension. There is also a loss of mercury in the form of mist, which is comparable with that given when many soluble vapours are passed through water—*e.g.*, NH_4Cl and SO_3.

Another system of condensation is that practised at Almaden in Spain. The mercury vapour and spent gases are passed through a series of **aludels** (Fig. 48), which are clay, pear-shaped vessels fitting one into the other. The line of aludels slopes first down from the kiln and then up the flue, thus ⌄

Fig. 48.—Mercury aludels.

a gutter being placed at the lowest point of the depression, so that the mercury condensed in either half of the series is received in a common channel. The members on the side of the series descending from the kiln, which receives the bulk of the mercury distilled, are provided with holes at the lower part which are stopped with sand, so that the mercury may filter through, and thus be removed, immediately on its condensation, from the current of hot gases passing through the aludels. The filtered mercury flows down a plane to the central channel. This system of condensation has the disadvantage of involving the making of numerous joints (often leaky) in connecting the aludels.

At New Almaden, in California, coarse ore furnaces for continuous working consist of an hexagonal base, at three alternate sides of which are the hearths. The ore chamber above the hearths is cylindrical. The ore, mixed with about 2 per cent. of coke, is charged in through a hopper at the top; and when it is

at a cherry-red heat the lower, spent, portion is raked out into the ashpit, and fresh ore charged. The content of mercury varies from 6 to 8 per cent. Condensation is sometimes effected in receivers of thin glass sheet set in wooden frames, this material being preferable to iron or earthenware, at temperatures below the boiling point of water, as it is not attacked by the condensed

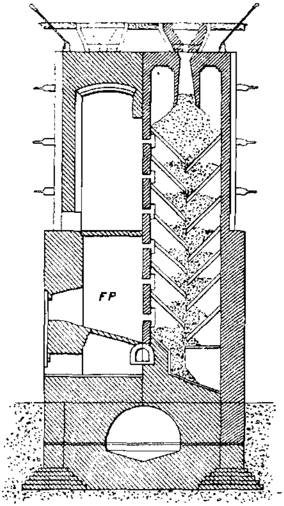


Fig. 49.—Granitza mercury furnace.*

sulphurous and sulphuric acid. "Fines" are treated, also continuously, in a vertical furnace which is fitted with inclined shelves (Fig. 49).

The fines are delivered from a hopper on each side of the middle partition of the furnace and fall from shelf to shelf,

* Coarse-grained ores are known as "granitza," and fine ores as "tierras."

turning over during their progress, so that every portion is exposed to the action of the hot air ascending from the hearths at the base of the kiln. The furnace usually consists of four shafts with a common fireplace.

In any of these processes mercurial soot (**stupp**) condenses in the chambers. It contains about 20 per cent. Hg, both as metal and as sulphate, etc. It is made into briquettes with lime (to decompose the sulphate) and re-worked.

Recent progress in the metallurgy of mercury has been in the direction of improved furnaces and more efficient condensing arrangements. Shaft furnaces, in which the ore and fuel come into direct contact, are now almost universal, and are of the continuous type, whereas formerly they were worked intermittently. The Californian furnaces described above (including the Granitza furnace) are also known as Scott furnaces from the name of their designer, and modifications of them are largely used throughout America. In Italy and elsewhere Spirek and Novak furnaces are mostly used, and are essentially the same in construction. The furnaces used for fine ores somewhat resemble the old Gerstenhofer calciner (see p. 241). One advantage of these modern shaft furnaces is that much less "soot" is produced than with the older type, especially when carbonised fuel (coke) is used. It is claimed that with their use the loss of mercury amounts to only 4 per cent. For fine ores which form much dust, and for lump ores which decrepitate, shaft furnaces are not suitable, and reverberatory furnaces are necessary. These are automatic, and are worked continuously. Muffle furnaces are now seldom used. Modern condensing arrangements take the form of a suitable combination of water-cooled tubes and chambers; Y-shaped stoneware tubes are commonly employed, while the condensers used with the Spirek furnaces are often made of iron and lined with cement or concrete to resist corrosion by acid liquors. To ensure more complete condensation, a low temperature and slow circulation of the gases in the condensers is maintained as far as possible. Another modern improvement is to utilise the waste heat of the cinders from the furnaces for raising the temperature of the air required for combustion and roasting.

2. **Removal of the Sulphur by Lime or Iron.**—The winning of mercury from cinnabar by distillation with iron takes place according to the equation—

$$HgS + Fe = Hg + FeS.$$

When lime is used to remove the sulphur the reaction is stated to be

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

In practice, the ore is mixed with iron or lime and heated in small bottle-shaped retorts, a number of which is set horizontally in a long gallery furnace. The mercury distils into receivers containing water, the condensation taking place much more readily than when the mercury vapour is diluted with inert gases, as in the case of the roasting process already described. Larger charges than can be distilled from these iron bottles are dealt with in iron retorts similar in shape to those used in the manufacture of coal gas (*q.v.*, Vol. II.). In the course of the distillation, finely-divided mercury and undecomposed sulphide come over with the main product, and are redistilled with more lime.

This method has been almost entirely abandoned, and is used only when a small quantity of rich ore has to be dealt with. It is not only costly for fuel and labour, but has a further disadvantage in that mercurial vapours are liable to be produced which are dangerous to the workmen employed.

The purification of crude mercury is usually a process of filtration, the metal being forced through wash-leather. Purification may also be effected by agitation with dilute nitric acid, the impurities being the first to dissolve. The metal is usually transported in wrought-iron flasks.

Properties and Uses of Mercury.—The specific gravity of mercury at 0° C., compared with water at 4° C. = 39·1° F., is 13·546 (*Volkmann*). It solidifies at − 39° C. = − 38° F., and boils at 357° C. = 675° F. The fact that its coefficient of expansion is remarkably uniform fits it for the construction of thermometers, and its high specific gravity for that of barometers. It is used for the extraction of gold and silver by amalgamation, and for the manufacture of looking glasses. For this purpose a sheet of tin foil is placed on a marble slab carefully levelled; a thin layer of mercury is then spread over the whole surface, the glass to be "silvered" is slid on to the prepared table and weighted, being left thus for some weeks. During the time of silvering the table is inclined to allow the surplus mercury to drain away.*

Mercury is also used in the preparation of various amalgams. Cadmium amalgam was formerly used as a stopping for teeth, and copper amalgam also serves as a plastic material. It becomes hard in a day or two (without expanding or contracting), but can be softened in boiling water. It has been used as a stopping for teeth, and as a cement for metals and china. A good deal of mercury is also employed in the electrolytic production of caustic soda.

* Looking glasses are now truly silvered with Ag, *cf.* p. 334.

SILVER.

SILVER ORES.—*Owing to the low heat of combination of* silver with oxygen it is not surprising that a good deal of the metal occurs **native,** although it is frequently alloyed with other metals, such as gold, copper, and, in rarer instances, mercury. It is sometimes associated with antimony as an antimonide, varying in composition from Ag_2Sb to Ag_6Sb. Cubic and octahedral crystals of silver, both massive and in dendritic forms, occur in many localities, but are especially abundant in Norway and Peru. Native silver may contain 90 to 99·8 per cent. Ag.

Silver sulphide (Ag_2S) occurs both alone (*argentite*) and together with antimony sulphide in the two forms—*brittle silver ore*, $5Ag_2S \cdot Sb_2S_3$, and *ruby silver ore*, $3Ag_2S \cdot Sb_2S_3$; *light red silver ore* corresponds with the latter, arsenic replacing antimony, and *polybasite* may be regarded as a mixture of the two, together with sulphide of copper. *Fahlore*, or *grey silver*, another important ore, is a mixture of antimony and arsenic sulphides with sulphides of silver, mercury, copper, zinc, and iron. It may contain up to 31 per cent. of silver.

Silver telluride, Ag_2Te, analogous with the sulphide, is found, as is also **silver selenide.**

Silver chloride (*horn silver*), AgCl, is found in considerable quantities in Chili and Peru, both massive and as scattered cubical crystals. It receives its metallurgical name from its appearance and texture. **Silver bromide** and **iodide** sometimes occur associated with the chloride.

Other Metallic Ores containing Silver.—As has been already stated, certain ores, notably galena, copper pyrites, and zinc blende contain small quantities of silver, and are worked for the recovery of that metal as an incident in the process of winning the main metal (*e.g.*, lead or copper) in the ore. The preliminary stages of the extraction of silver from such ores—*i.e.*, its concentration before recovery—have been described in the chapters dealing with the ores themselves. The largest portion of the world's supply of silver comes from the United States, Mexico, and South America. Australia (notably from Broken Hill) contributes a large quota.

WINNING OF SILVER FROM ITS ORES.—1. **General Principles.**—Silver is one of the most easily reducible metals, owing to the circumstance that its oxide is split up at a red heat, as indeed is illustrated by the fact that it may be reduced in the laboratory from a salt, such as silver chloride, by heating with

an alkaline flux—*e.g.*, sodium carbonate—without a reducing agent, the reaction taking place on the following lines:—

$$2AgCl + Na_2CO_3 = Ag_2O + CO_2 + 2NaCl.$$
$$Ag_2O = 2Ag + O.$$

On a large scale, ores are seldom rich enough in silver or sufficiently free from other metals to make such direct extraction a practicable method. Silver has, however, a special tendency to dissolve in other metals and in metallic sulphides, hence it can be conveniently concentrated by fusion of the ore with a flux, and, if necessary, some other ore to provide the solvent metal or sulphide. Examples of this, when the ore is particularly poor, have already been given under lead and copper smelting (*q.v.*). In the case of lead the silver concentrated in this way is extracted by again taking advantage of the fact that silver oxide does not exist at a red heat, so that the lead can be oxidised and removed, leaving the silver as metal. In the case of the copper sulphide the process depends on the circumstance that silver shows its similarity to the alkali metals by the stability of its sulphate (Ag_2SO_4), which is formed on roasting the matte, and is not decomposed by a temperature sufficient to decompose the copper sulphate which is simultaneously formed. Another instance of the collection of silver in a solvent is afforded by the use of mercury at the ordinary temperature, corresponding with that of lead at a high temperature. In this case, as no decomposition of a silver salt by heat can be employed, some other means of obtaining the silver as metal is necessary. The mercury will subserve this purpose as well as act as a collecting agent.

Another general principle applied in methods of silver extraction is the ease with which silver chloride can be formed by roasting silver ores with salt, the stability of the chloride thus produced and its solubility in solutions of other chlorides or of thiosulphates. Alkaline cyanide solutions have also been used successfully in recent years for the extraction of silver from its ores exactly as in the treatment of gold ores. A precipitation of the dissolved silver as metal or as sulphide serves for its recovery when thus extracted.

2. **Dry Processes for Winning Silver.**—(*a*) **Extraction with Lead as a Solvent.**—The production of ordinary argentiferous lead (from galena) has been already described (see *Lead*). When the silver is present in sufficient quantity to cause the ore to be classed as a silver ore, the reduction is effected in blast furnaces to the exclusion of those of the reverberatory type. The charge is a mixture of ores, fuel, and fluxes, and usually contains 10 to 12 per cent. of lead and 8 to 15 per cent. coke. With poor ores

the silver is sometimes collected in a pyrites matte by adding this mineral to the furnace charge; the resulting matte is roasted in heaps, and fused with richer ores, whereby an additional proportion of silver is extracted; the metal may be now transferred to lead by running the matte into a bath of metallic lead; the silver sulphide in the matte is thus reduced and the silver retained by the lead. Argentiferous lead ("base bullion") containing upwards of 0·1 per cent. Ag (30 ozs. per ton) can be cupelled directly, but poorer metal must be enriched by one of the processes of concentration (Parkes or Pattinson), described under *Lead*. When concentration is adopted, much richer leads are cupelled—*e.g.*, such as contain 300 ozs. of silver per ton. The works process of cupellation combines the features of the laboratory processes of scorification and cupellation, the lead

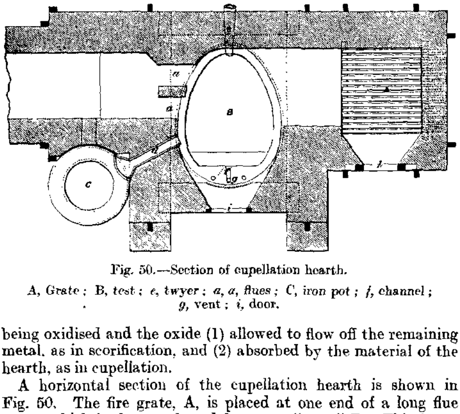


Fig. 50.—Section of cupellation hearth.
A, Grate; B, test; e, twyer; a, a, flues; C, iron pot; f, channel; g, vent; i, door.

being oxidised and the oxide (1) allowed to flow off the remaining metal, as in scorification, and (2) absorbed by the material of the hearth, as in cupellation.

A horizontal section of the cupellation hearth is shown in Fig. 50. The fire grate, A, is placed at one end of a long flue across which is the egg-shaped frame, or "test," B. This frame was formerly filled with bone ash, and serves to contain the lead to be treated. At the present time marl, which is cheaper, or a mixture of cement and fireclay, is used instead of bone ash, especially for the first stage of the process. The twyer, e, supplies a blast of air which plays upon the surface of the lead. The

flame of the fire passes across the test, the products of combustion passing away by the flues, *a a*. From 4 to 5 cwts. of the lead are melted in an iron pot, C, and run through the gutter, *d*, on to the test. When its surface becomes covered with fused litharge the blast is turned on, and the melted oxide is driven in waves over the surface of the lead, escaping through the channel, *f*, and the vent, *g*. The progress of the operation is watched through the door, *i*, and fresh lead is charged in from time to time until the enriched alloy contains about 8 per cent. of silver. It is not profitable to concentrate this further on the same test, inasmuch as a continually increasing proportion of silver passes into the litharge, and is troublesome to recover from the whole quantity. At this stage, therefore, the metal is tapped by making a hole in the floor of the test. It is transferred to a new test where the process is continued until the surface of the metal becomes bright, indicating that no further oxidation is taking place, and that silver remains. The silver is either tapped or allowed to solidify on the test. This silver contains from 99·7 to 99·8 per cent. Ag, and is refined by again heating it on a cupel, the impurities (save gold)—*e.g.*, Cu, Pb, Bi—being oxidised and absorbed. The litharge, especially the last portions rich in silver, is reduced, concentrated by pattinsonising and re-cupelled. The cupels are broken up and smelted for the recovery of lead and silver.

Rich bullion, such as that obtained in the Parkes process, can be completely cupelled in one operation. In modern practice, however, two operations are often used, the advantage of the double process being that the first stage can be carried out in a large water-cooled cupel, which lasts much longer than the ordinary test.

There are two methods of conducting the cupellation process—the English and the German. The English furnace is characterised by a comparatively small movable hearth and a fixed roof, the lead being added at intervals. The German furnace is much larger, is usually circular, and has a fixed hearth and movable roof. The cupel is made of marl, containing 65 per cent. calcium carbonate, 30 per cent. clay, and 5 per cent. magnesium carbonate and iron oxide. The whole of the charge is placed on the cupel at once, and the process is usually completed in one operation.

(*b*) **Extraction with Copper Matte as a Solvent.**—In the case of this process the silver is a bye-product, the copper being the metal primarily to be won. As already described under *Copper* (p. 25[illegible]), a matte containing cuprous sulphide and some iron sulphide and silver sulphide (0·5 per cent. Ag) is roasted,

the iron and copper being converted into oxides and the silver into sulphate (this salt being very stable, as already mentioned). To avoid decomposing silver sulphate the roasting must be stopped before a sample ceases to give a blue solution (presence of $CuSO_4$). The silver sulphate is leached out with water containing a little sulphuric acid (to prevent the formation of basic salts) and the silver precipitated by copper, the copper being recovered by means of iron.

The precipitated silver is washed with dilute sulphuric acid to remove remaining basic copper salts, pressed into blocks, fused and refined by an oxidising roasting (sometimes with the addition of saltpetre) in a reverberatory furnace.

3. **Wet Processes for Winning Silver.**—(A) **Extraction of Silver by the Use of Mercury for Collecting and Dissolving it (Amalgamation Processes).**—In amalgamation processes reduction of the silver in the ore to the metallic state—a necessary preliminary—is most readily effected when the silver is in the form of chloride, on which account the ores containing sulphides, etc., are either roasted with salt,* or, if fuel be scarce, treated during the process with copper chloride (in the form of a mixture of salt and copper sulphate) which is capable of reaction with silver sulphide at a sub-tropical temperature.

(1) *Amalgamation Process with Iron as a Reducing Agent.*—(*a*) *Barrel Process.*—This method, which is now obsolete, is a typical amalgamation method, and may be briefly described.

The crushed ore is roasted with salt to convert the silver into chloride, and charged, together with scrap iron, into rotating barrels with enough water to make a thin paste. After some hours' rotation, mercury and sometimes a little copper sulphate are added and rotation is continued for a longer period. The barrels are then filled with water, and the mercury, holding silver in solution, run off from the bottom. The silver amalgam is distilled in iron retorts resembling gas retorts (sometimes under reduced pressure) and the silver recovered.

(*b*) *Pan Amalgamation* or *Washoe Process.*—In this method the finely stamped ore is graded by settling, it being essential that the subdivision shall be fine. It is then ground in an iron pan with iron mullers, with mercury and sufficient water, the pan being heated to about 85° C. = 185° F. by steam. The iron of the pan and mullers, in conjunction with the mercury, reduces the silver to metal and an amalgam is formed. It is found that even sulphide ores can be worked in this way, a probable reason

* In such chlorinating roastings the sulphide is first converted into a sulphate which then reacts with the sodium chloride, giving sodium sulphate and a chloride of the metal under treatment.

being that the ore is in a fine state of division and the temperature is high. Occasionally, however, such ores are subjected to a chlorinating roasting, the amalgamation being more rapid and effective after this treatment. Sometimes chlorinating agents—*e.g.*, copper chloride—are added to the charge, their action being similar to that described under the Mexican process (*v.i.*). The contents of the pan is washed into a separator. This is a tub, the bottom of which slopes from the centre to the circumference, and is traversed by a number of rakes. There being enough water in the tub to allow of a fractional subsidence, the mercury and amalgam collect on the bottom, and are run off, strained, and distilled in the usual way.

A continuous process is also in use in which the pulp passes automatically through a series of pans, the first two or three of which are arranged for grinding (*Boss process*).

(2) *Amalgamation Process with Mercury as a Reducing Agent* (*Mexican Process*).—Crushed ores are ground to powder in a primitive edge-runner mill, together with a little mercury if free gold or silver be present. The ground ore, in the form of a mud, is spread on a floor and trodden by mules, with about 4 per cent. of common salt. Mercury and "magistral" (*i.e.*, roasted copper pyrites, consisting chiefly of $CuSO_4$, $FeSO_4$, CuO, and Fe_2O_3) are added, the former to the extent of about six times the silver content of the ore. After a further intermixture a hot solution of copper sulphate, in proportion varying with the amount of sulphur and arsenic in the ore, is run on to the heap. Copper precipitate may be advantageously added, probably because its reducing effect on the silver supplements that of the mercury. The chemistry of this and like processes has not been thoroughly worked out, but the chief reactions occurring appear to be (*a*) the reaction of copper sulphate with sodium chloride, giving cupric chloride and sodium sulphate; (*b*) that of cupric chloride on silver sulphide, giving cupric sulphide and silver chloride, the latter then dissolving in the solution of sodium chloride; in a similar way cuprous chloride can decompose silver sulphide, forming silver chloride and metallic silver. Ferric chloride is also present, and reacts with silver sulphide, forming silver chloride, ferrous chloride, and free sulphur; (*c*) the reduction of silver chloride to silver by mercury, aided by copper, with the formation of mercurous chloride and cuprous chloride: and (*d*) the formation of silver amalgam by the interaction of silver and mercury. When these changes are complete, more mercury is added to the charge, and the whole stirred with water in a tank; the silver amalgam settles, is run off, and filtered through canvas to separate the excess of mercury from the

semi-solid amalgam. The amalgam is distilled, frequently by the simple process of heating it in a series of vertically disposed trays covered by an iron bell standing in water; the upper part of the bell is encased in a furnace, and the mercury condenses in the water reservoir.

The Mexican process as just described is now becoming obsolete, having been greatly modified in recent years by the introduction of fine grinding in tube mills in conjunction with the cyanide process (v.i.).

Other modifications of the amalgamation process are the *Krönke* and *Francke* processes. The former depends on the use of a hot solution of cuprous chloride in common salt for decomposing the refractory silver compounds, the operation taking place in revolving wooden barrels. The silver is finally reduced by means of an amalgam of zinc or lead. In the *Francke process* the ore, after chloridising roasting, is made into a pulp with a 10 per cent. solution of sea salt, and introduced into wooden barrels provided with copper bottoms and side plates. Mercury is added at intervals, and the mixture is heated by steam and agitated by mullers. The chemical reactions which take place cause copper to be dissolved, while silver chloride and silver are amalgamated.

(B) Extraction of Silver by Dissolution and Precipitation.—In the preceding processes, both dry and wet, concentration by collection of the silver in a solvent (lead and mercury) has only been possible after reduction to the metallic state. In like manner, in the processes about to be described (excluding the cyanide process, which is considered later), the silver has to be converted into chloride before its dissolution and extraction. Only two solvents are commonly employed—viz., a strong solution of sodium chloride and one of sodium or calcium thiosulphate.

(*a*) *Extraction with Sodium Chloride and Precipitation by Copper (Augustine's Process).*—Both ores and copper mattes are first roasted alone, by which process the bulk of the sulphides is converted into oxides, but owing to the stability of silver sulphate (*v.s.*), most of the silver sulphide is converted into this salt. The roasted material thus contains most of the copper (and iron) as oxide, but a portion as basic sulphate; most of the silver is as sulphate, but a part still as sulphide. On re-roasting with salt, the oxides are unattacked, whilst the sulphates of copper and silver are converted into chlorides by double decomposition. The residual silver sulphide, when roasted in the presence of sodium chloride, undergoes the change characteristic of a chlorinating roasting, forming, first, sulphate, and

then, by double decomposition, silver chloride and sodium sulphate. In the Ziervogel process (see *Copper*, p. 255), the whole of the silver sulphide must be converted into sulphate in order to be extractible, necessitating very careful roasting, whereas in the present case, residual silver sulphide from the first roasting is not lost because afterwards transformed into chloride. The final product, whether from matte or ore, consists of copper oxide (and ferric oxide), silver chloride, and sodium sulphate. From this the silver chloride is extracted by leaching with a hot, strong solution of common salt, in which it is fairly soluble.* The brine containing silver chloride is filtered through a layer of cement copper (see p. 255), the silver being precipitated and the copper going into solution as chloride. The cement silver is washed with hydrochloric acid and refined in the usual way. The Augustine process is now seldom used, except occasionally in conjunction with the Patera process (*v.i.*).

The principles of this process have been applied to the treatment of argentiferous copper bottoms (now generally refined, with recovery of silver, by electrolysis—see p. 260), which are granulated, roasted to oxide, ground and roasted again with ferrous sulphate, which acts in the same way as the sulphate resulting from the roasting of a matte (detailed above). The product is leached with water as in the Ziervogel process (p. 255), and the residue, containing silver as sulphide, is roasted with salt and extracted in the manner proper to the Augustin process.

The recovery of silver from burnt pyrites by the *Claudet process* resembles the Augustin as far as the obtainment of a solution of silver chloride in sodium chloride is concerned, but the silver is separated by precipitation with an iodide, the silver iodide being collected and reduced with zinc, yielding the silver. The zinc iodide thus formed is used for precipitating a fresh portion of the chloride solution.

(*b*) *Extraction with a Hyposulphite* (*thiosulphate*) *and Precipitation as Sulphide* (*Patera's Process*).—The preliminary operations do not differ in principle from those already mentioned as preceding extraction with sodium chloride. Inasmuch as in this process the solution of silver chloride is to be treated with sodium sulphide (*v.i.*), it is advantageous to wash the product of the chlorinating roasting with water, in order to remove the chlorides of copper, zinc, iron, etc., which would otherwise be precipitated as sulphides, together with the silver sulphide. The residues from this washing are treated with a cold solution of sodium thiosulphate (or calcium thiosulphate, as in the *Kiss process*), the

* 100 parts of water saturated with sodium chloride dissolve 0·4 part of silver chloride at 100° C. = 212° F.

silver chloride being thus brought into solution. Sodium sulphide is added to the liquor until no further precipitation takes place, and the silver sulphide is roasted in muffles, charged into a bath of molten lead, and cupelled, any silver sulphide which is not thus decomposed being reduced by iron in crucibles (see *Reduction of galena by iron*, p. 273). Care is taken to add only just sufficient sodium sulphide to precipitate the metals as the liquors are used again for leaching. When a solution of a double hyposulphite of sodium and copper (*Russell process*) is used, silver sulphide is said to be attacked, the silver being dissolved as the double hyposulphite of sodium and silver, and the copper precipitated as sulphide. The tailings from the lixiviation of a chlorinating roasting, containing unattacked silver sulphide, may be treated by this method.

The Cyanide Process has practically displaced all other methods for treating silver ores in Mexico, and is essentially the same as that employed for gold extraction (*q.v.*). The ore is ground in stamp and tube mills, and treated by percolation and agitation with a solution of potassium cyanide. The latter is much stronger than that used for gold ores, and may contain as much as 1 per cent. of KCN. The primary reaction is represented by the following equation, the silver being dissolved as a double cyanide :—

$$Ag_2S + 4KCN = 2KAg(CN)_2 + K_2S.$$

The reaction is reversible, and an equilibrium stage is reached when a certain proportion of potassium sulphide has been formed. The following secondary reactions are also important :—

$$2K_2S + 2O_2 = K_2S_2O_3 + K_2O.$$
$$K_2S_2O_3 + K_2O + 2O_2 = 2K_2SO_4.$$

These involve an absorption of oxygen, and show that aëration plays an important part in this method of extraction. The solution is separated by means of vacuum filters, and the silver precipitated by zinc shavings or zinc dust. The black silver slimes are finally briquetted, smelted with fluxes, and cupelled in the usual way.

The refining of silver, as has been already stated, may be performed by roasting, supplemented by the action of oxidising fluxes—*e.g.*, saltpetre. The electrolytic silver refining process has made rapid headway during recent years, especially in connection with the working up of the slimes obtained in copper refining (*q.v.*, p. 260). In the *Moebius process* the crude silver is cast into plates, which are made the anodes of a cell containing a mixture of silver and copper nitrates, together with a small proportion (under 1 per cent.) of free nitric acid. The anodes

are enclosed in muslin bags, which retain gold, platinum, and lead (the last as PbO_2), while silver and copper are dissolved, the former alone being deposited on the cathodes, which consist of thin silver plates. The silver is obtained in a rough crystalline form, and is removed from the cathodes by scraping with wooden laths. Its purity may be as high as 99·95 per cent. In an improved form of the Moebius cell a revolving sheet cathode is wholly immersed in the electrolyte, and the silver crystals deposited on this are automatically removed by a scraper at one end of the vat. The anodes are placed in porous trays above the cathode, and can be examined without stopping the process.

The *Balbach process*, as used at Newark, U.S.A., is essentially the same as that just described, and differs from it mainly in the construction of the cell.

Dietzel has worked out a process for separating copper, silver, and gold in alloys, which has been in use for some years at Pforzheim. A solution of copper nitrate containing free nitric acid is employed as the electrolyte in a vat divided by a diaphragm into two compartments. This solution dissolves silver and copper from the alloy anodes, and the silver thus dissolved is precipitated chemically by the action of copper scrap in an adjacent vessel, the regenerated copper nitrate being returned to the cathode compartment of the cell, where the copper is deposited on pure copper sheet cathodes. The gold is obtained as an insoluble residue from the anode compartment.

A. G. Betts has patented a new method for refining silver, in which the electrolyte contains 4 per cent. of silver as silver methyl sulphate, and 4 per cent. of methyl sulphuric acid. An addition of carbon disulphide is found to harden the deposit of silver. The latter is both hard and solid, unlike the rough crystals which cause such difficulty in operating the Moebius and Balbach processes.

Properties and Uses of Silver.—Silver has a specific gravity of 10·53, and a fusing point of 960° C. = 1,760° F. It is the best known conductor of heat and electricity. It is characterised by its stability in air free from sulphureous gases. Molten silver absorbs 22 volumes of oxygen from the air, and the gas is given off again with much vigour during solidification (the so-called "spitting" of silver). It may be prevented by the addition of a small quantity of some oxidisable metal—*e.g.*, magnesium. It is probable that molten silver forms the oxide Ag_2O, which is stable at high temperatures, although it is instantly decomposed at a red heat. For use in coinage and ornaments it is alloyed with copper, which lowers its melting point, prevents it from spitting, and makes it harder without sensibly impairing its

malleability or altering its colour. Thus, English sterling silver contains 92·5 per cent. Ag and 7·5 per cent. Cu. In most other countries the coinage contains 90 per cent. silver. In the pure state silver is largely used for silver-plating, being deposited electrically from the double cyanide of silver and potassium. The deposit from such a bath is dead-white, and requires to be scratch-brushed. By adding a little carbon disulphide, however (1 part in 50,000) a bright deposit of silver is obtained. An alloy of silver and cadmium, containing 10 per cent. or more of the latter metal, has been deposited electrolytically, and is less easily tarnished than pure silver. On account of the fact that silver can be deposited as a brilliant adherent film on glass, mirrors made with an amalgam of tin and mercury (see *Mercury*, p. 323) have been largely replaced by those prepared by allowing a solution of ammonio-tartrate of silver to deposit the metal on a clean glass surface, the reduction taking place when the solution is warmed. Silver-tin alloys containing from 40 to 60 per cent. of tin, and silver-platinum alloys containing from 25 to 35 per cent. of platinum are used in dentistry. The former are mixed with about an equal weight of mercury; the pasty amalgam thus formed becomes quite hard in from 24 to 48 hours, due to some molecular change. The platinum alloys are hard, but ductile, and are also used in jewellery. The alloy containing 33·3 per cent. of platinum has also been used as a standard of electrical resistance.

GOLD.

Sources of Gold.—Gold is nearly always found native, alloyed with more or less silver. It occurs massive as nuggets, weighing from a fraction of an ounce to many pounds, and in veins distributed through quartz, generally associated with sulphide minerals—*e.g.*, pyrites and galena. In places where such veins have undergone a process of weathering, finely-divided alluvial gold is found in the beds of rivers now flowing or of ancient date. For the most part these gravelly deposits are loose in texture and easily disintegrated by water, but are sometimes found agglomerated in masses which have the appearance of bed-rock. In the above cases the true gangue is of a siliceous character, and the gold is comparatively easy to extract. There is, however, a considerable quantity of gold, the gangue of which consists of pyrites or galena with which the gold is so intimately associated as to have given rise to the opinion that it also is as sulphide. This does not appear to be the case, but tellurides of

gold (*calaverite*, $AuTe_2$) and silver are known. Gold is also a bye-product of the winning of other metals, notably silver, copper, and lead. The chief gold-producing countries are Africa (Transvaal, Rhodesia, and West Africa), Australia, America (California), and Russia. Gold is widely distributed in the western mountains of North America, alike in Mexico, the United States, and Canada, reaching as far north as the Klondyke district. The chief European mines are found in Hungary. Gold is also widely distributed in Asia, especially in Borneo, China, Japan, Korea, and the Dutch East Indies. The composition of native gold falls between the limits gold 64·77 to 99·2 per cent., silver 35·23 to 0·43 per cent., iron and other minerals up to 0·28 per cent.

Winning of Gold.—The bulk of the world's production of gold is obtained by comparatively simple processes, depending (*a*) upon the high specific gravity of the metal (19·32 when pure), and (*b*) upon the ease with which it is taken up by mercury. Certain ores do not give a satisfactory yield on treatment with mercury, and are known as "refractory" ores, as distinguished from "free milling" ores. The tailings from the amalgamation process often contain heavy minerals—*e.g.*, pyrites and galena, which carry gold. They are, therefore, treated by concentration, and the concentrates smelted with lead or roasted and treated by the chlorination process (*v.i.*). Refractory ores are treated by smelting, cyaniding, or chlorinating, according to circumstances. The gold obtained by any of these processes is melted, cast into bars, and refined. The washing and amalgamation of gold are mechanical processes, which will be dealt with here to illustrate typical methods for the concentration of ores generally by mechanical means. Such processes for winning gold as depend upon strictly chemical principles will be described later.

Concentration of Gold and Other Ores.—The fundamental principle underlying the mechanical concentration of gold ores is that when two particles of identical shape and equal volume but different weight are allowed to fall through a resistant medium, that which has the greater weight will fall faster than the other. It follows from this that the difference in specific gravity of two substances is an index of the ease with which they may be separated in this manner, provided the conditions of identity of shape and volume be maintained. But by increasing the size of the particle of lower specific gravity it will eventually fall as fast as that of the higher specific gravity, because the surface it exposes to the resistance of the medium is smaller relative to the impelling force (its weight). Also by altering the shape of the particle of lower specific gravity, so that it presents a smaller surface for a given volume than does the particle of higher specific

gravity, a similar compensating effect will be obtained. Thus it is, that, though in ideal concentration the particles will be of identical size and shape and of different specific gravities, yet, in practice, imperfection of sizing and irregularity of shape necessitate large differences in specific gravity to compensate for these disturbing factors. The great difference in the specific gravity *of gold (19·3) (native gold containing silver may have a specific* gravity of 17 or less) and siliceous gangue (2·7) leaves a larger margin for providing this compensation than is available in most other cases.

Winning Alluvial Gold.—For a long time the mere washing of auriferous sands in pans where the necessary suspension was attained by *hand-shaking, sufficed for winning gold.* As no sizing was attempted, only a crude separation was thus possible. The "cradle," which is an inclined trough set on rockers, constitutes a development of the pan.* It is plain that the process of permitting particles which are to be separated, to fall through a resistant medium, can be replaced by the plan of causing the medium to flow over the particles in a thin layer. An additional cause for separation here occurs—viz., the difference of velocity of the upper layer of a thin stream of water and the lower layer in contact with the channel through which it flows. This difference of velocity will allow of a still larger deviation from identity of size and shape, because the larger particles will stick up into the upper layer of the stream, and their upper parts will be exposed to its full force, so that they will tend to be carried on in spite of their size.

This principle is applied by washing the crushed ore or auriferous sand down an inclined plane with a thin stream of water. The separation is aided by rendering the floor of the channel rugose. Thus, the inclined channel is sometimes covered with a blanket or by "*riffles*"—*i.e., strips of wood dividing it into* chequer work. In recent years perforated iron plates and "expanded metal" have been largely used for this purpose. When working auriferous gravel on a large scale, the method adopted is to direct a powerful jet of water on to the slope, the surface soil of which consists of the gold-bearing material, the process being termed "hydraulic mining." The debris is conveyed down a long sluice consisting of a series of wooden troughs set at a gradient of about 8 to 18 inches in 12 feet.

The bottom of the troughs is covered with riffles, in which the gold collects. The collection of the gold is aided by putting mercury in among the riffles. Methods of catching gold by means

* In this case a rough sizing of the gold-bearing gravel by means of a riddle at the head of the cradle is generally adopted.

of mercury may be combined with all ordinary washing processes.

The use of "dredges" for winning alluvial gold has rapidly extended during the last few years. The dredges used are flat-bottomed boats, with machinery for raising gravel from the bottom of a stream, hoisting it on board, washing it over inclined tables to save the gold, and finally dumping the tailings overboard at the stern.

Winning Gold from the "Ore."—By "ore" is here meant any rock-bearing gold, hard enough to require comminution by other means than mere washing ("quartz mining"). The chief processes requisite are :—

1. **Comminution.**—The ore is first put through a stone-breaker and then pounded in a stamp mill (Fig. 51). This consists of a series of vertical pestles of great weight and shod with iron, alternately raised and allowed to fall by a shaft and cam, C, operating a tappet, T. The stamp, ST, with its head, S, strikes upon an iron block or shoe, D, in the mortar, M, into which the ore is fed. The mortar is covered and is provided with a hopper on one side for receiving the broken ore, and a rectangular opening opposite to this in which a screen, SC, to retain coarse fragments, is fitted. Most of the crushing is generally done dry and a stream of water is then let in, the motion of the stamps being continued. The crushed rock is thus churned with the water into a thin mud (*slimes* or *pulp*), the gold, if in large particles, sinking to the bottom of the mortar, and being collected by mercury in the channel surrounding the block, D. The finer gold is splashed up and either flows through the screen with the slimes, or adheres to amalgamated copper plates which line the sides of the mortar.

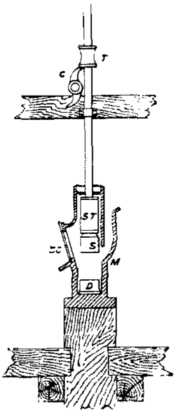


Fig. 51.—Stamp.

T, Tappet; C, cam; ST, stamp; S, stamp head; D, shoe; M, mortar; SC, screen.

2. **Amalgamation.**—That part of the gold which is not caught in the stamps is collected by concentration and amalgamation in the following manner :—In passing into the sluices the slimes

first traverse amalgamated copper plates where much of the gold is retained, a further portion being caught by the blankets with which the sluice is lined, from which it is afterwards washed and collected in mercury by the aid of an amalgamating pan. After flowing through the sluices, the main slimes, together with those from the amalgamating pan, pass into some form of "rubber," in which they are triturated between iron surfaces in order to brighten the surface of the particles of gold, and thus enable them to be amalgamated, such amalgamation being often performed in the rubber, which is fitted with amalgamated copper plates.

The system of amalgamation inside the battery by the sprinkling of mercury in the mortar and the use of internal amalgamated plates is now falling into disuse. Moreover, ball-mills and roller-mills are now frequently used instead of stamp batteries, especially for dry crushing.

3. **Concentration Proper.**—It will be noted that during the passage through the sluices and over the copper plates concentration as well as amalgamation takes place. A certain amount of finely-divided gold will, however, escape with the slimes from the rubber, and this may be further concentrated in a systematic manner. The tailings from stamp battery amalgamation are now usually treated by the cyanide process (*v.i.*) without any previous concentration. When a process of concentration is used it is carried out by first sizing the material in "pointed boxes" having a V-shaped bottom in which there is a slit to permit of the passage of those grains which are of such a size and specific gravity as to sink. By using a series of such boxes of increasing cross-section the flow of water bearing the slimes will at first be too rapid to allow of any but the largest equal-falling grains to reach the bottom, become less rapid as it proceeds, and depositing successive fractions of decreasing size. The sized sands are then concentrated in sluices as before. Further concentration is effected in inclined rockers, buddles,* and tossing tubs.†

In modern practice a Frue vanner serves for concentrating the slimes. This consists essentially of an endless sloping rubber belt carrying a stream of water, which flows in the opposite direction to that in which the belt is moved. The separating effect of the stream is here aided by the opposite motion of the belt, which also receives an oscillatory movement that favours segregation. The first-falling particles are thus collected at one

* The buddle is generally a round box with a coned bottom, sloping towards the circumference, over which brushes, set on radial arms, are carried.

† Circular vessels provided with rotating agitators.

end of the machine, whilst the remainder flows off at the other end.

It will be seen that during these treatments a large proportion of the gold has been collected in mercury in the stamps and sluices, and another portion as concentrates (associated with pyrites). The gold amalgam is collected and distilled in the manner already described for silver (p. 330). After squeezing in wash leather the mercury is distilled off in cast-iron retorts. The *residue contains gold, silver, base metals, sulphides,* and some mercury. It is melted in graphite crucibles with borax, soda carbonate, nitre, and sand. A fusible slag is formed which contains the sulphur and the greater part of the base metals as silicates. The molten material is poured into ingot moulds, and the slag and bullion afterwards separated.

Before leaving the subject of amalgamation it may be said that *the cleanliness of the mercury is essential for its proper utilisation.* As it tends to become foul by use it is "quickened" by stirring it with a solution of potassium cyanide or dilute acid, but is best restored to purity by distillation. Mercury containing a small quantity of sodium is said to be efficacious in keeping the bulk of the mercury active as a solvent. The concentrates (*v.s.*) are roasted to remove sulphur, and are either amalgamated or more usually chlorinated (*v.i.*) for the recovery of the gold which they contain. Rich concentrates may be smelted with lead and cupelled.

Winning of Gold by Chemical Processes.—1. **Chlorination.**—The roasted ore, usually in the form of concentrates, is moistened and put into a wooden tub lined with some chlorine-resisting material, such as tar, and provided with a false bottom beneath which a pipe from a chlorine still opens. The tub and the chlorine still are shown in Fig. 52. The attack is continued for some hours in the closed tub, and at the end of the time water is poured in to cover the ore, and the solution of gold chloride filtered. The chlorine should be washed free from hydrochloric acid, so that it may attack only the metals present and not the oxides—*e.g.*, ferric oxide from roasted pyrites—nor the sulphides remaining from imperfect roasting, as in the last case H_2S would be evolved and precipitate gold. The necessity for the absence of sulphides makes it requisite that the roasting should be as complete as possible; when alkaline earths—*e.g.*, lime—are present, a chlorinating roasting by the addition of salt is advisable, as otherwise such materials lead to the consumption of chlorine in extracting the gold. The dissolution of the gold is sometimes aided by pressure applied either to the chlorine or hydraulically to the solution in the extracting vessels, and by

the use of revolving or tumbling cylinders to agitate the ore during extraction. In the latter case it is usual to generate the chlorine inside the barrel itself by means of sulphuric acid and bleaching powder. However obtained, the solution of gold chloride is precipitated by a solution of ferrous sulphate—

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3$$

by SO_2, or by filtration through charcoal. The cause for the reducing action of the last-named is obscure. In the barrel process it is customary to precipitate the gold by means of sulphuretted hydrogen, and the sulphide of gold is filter-pressed, roasted on iron trays, and melted with fluxes. If base metals are present in any quantity, ferrous sulphate is used as the precipitant. The chlorination process, although still used for

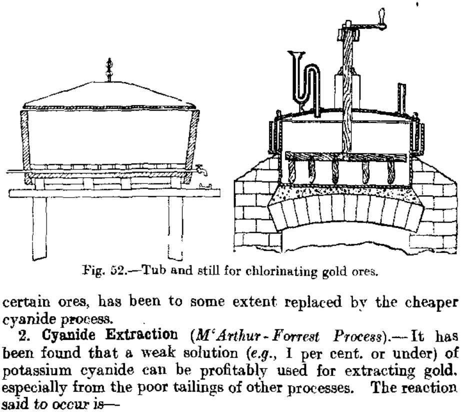


Fig. 52.—Tub and still for chlorinating gold ores.

certain ores, has been to some extent replaced by the cheaper cyanide process.

2. **Cyanide Extraction** (*M'Arthur-Forrest Process*).—It has been found that a weak solution (*e.g.*, 1 per cent. or under) of potassium cyanide can be profitably used for extracting gold, especially from the poor tailings of other processes. The reaction said to occur is—

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH,$$

the presence of oxygen or some negative element or radicle being essential. Thus bromine may be used in the form of cyanogen bromide.

Ores generally need some preliminary treatment before extraction. Tailings from other processes are first sized in the

manner described under "concentration" (p. 338), the sands and slimes being treated differently, as described below. Latterly, it has been found advisable to reduce these tailings to a fine slime in tube mills, to pass the product over shaking amalgamated copper plates, and then to extract it with cyanide solution. Refractory ores may need roasting before extraction, and for this purpose automatic furnaces are now almost universal. Occasionally the ores are first washed with water to dissolve out any soluble matter, or with a solution of soda or lime to neutralise any acid that may be present due to the decomposition of pyrites, etc. After this preliminary treatment the ore in the form of sands is treated by percolation with a solution containing 0·1 to 0·35 per cent. of KCN in large vats of wood, iron, or cement, holding 500 to 600 tons, and provided with false bottoms covered with canvas. A "strong" and a "weak" solution are often applied in succession, the time of treatment by the strong solution varying from 24 to 48 hours. Three or four additions of solution are usually sufficient for complete extraction, and the ore is often aërated between each addition. On the other hand, fine slimes are treated by agitation with a more dilute solution (containing 0·01 per cent. KCN), and afterwards separated either by decantation or by means of filter presses. The liquor thus obtained is run into troughs containing zinc shavings coated with precipitated lead by pickling in a solution of lead acetate. The zinc-lead couple thus formed is found to be a more effective precipitant of gold than pure zinc. The lead itself, however, remains unchanged, the gold being precipitated according to the following equation :—

$$2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au.$$

"Zinc dust" is also used for precipitating gold from cyanide solutions. The residue containing the precipitated gold is washed and treated with dilute sulphuric acid or sodium bisulphate, in order to dissolve excess of zinc and to decompose any cyanide present (*e.g.*, zinc cyanide, which may be deposited as a white powder). The slimes are washed with hot water, filtered, dried, and fused with fluxes (soda carbonate, borax, and sand) in graphite crucibles. A more recent process, which is said to effect a saving in cost, and to be attended by less loss of gold, is *Tavener's* lead smelting method, in which the slimes, after filter-pressing, are fused with litharge, fluxes, and sawdust in a reverberatory furnace for the production of a lead bullion containing 8 per cent. of gold, which is afterwards cupelled.

An alternate plan of recovery consists in running the cyanide liquor into a tank filled with iron anodes and sheet lead cathodes,

upon which the gold is deposited by a feeble current. The cathodes when loaded with gold are removed and cupelled. The anodes are enclosed in bags to retain any Prussian blue formed by the action of the cyanide upon them.

Telluride ores, such as those of Colorado and West Australia, need special treatment. Two methods are largely used for dealing with these ores. In the **Diehl process** the ore is crushed with water in stamp batteries, amalgamated, concentrated, and the tailings separated into sands and slimes. The concentrates are dried, roasted, and sent back to the crushing mill. The sands are reground in tube-mills, and the whole of the fine material is then agitated with cyanide solution to which some bromo-cyanide is added, and filter-pressed. In the **Marriner process** the ore is crushed dry in roller-mills or ball-mills, and roasted dead. The product is ground with mercury and cyanide solution in pans, and the tailings are agitated with dilute cyanide solution and filter-pressed.

3. **Collection of Gold in a Pyrites Matte.**—The auriferous pyrites is smelted with an alkaline flux (*e.g.*, limestone) to remove quartz; about half the sulphur of the pyrites is volatilised and a matte of ferrous sulphide obtained. This is roasted and smelted with a fresh quantity of pyrites, the siliceous matter of which fluxes the iron oxide formed during the previous roasting. The series of processes is repeated until a matte rich in gold is obtained, when it is again roasted and fused with lead which dissolves out the gold, and is cupelled for the recovery of the precious metal.

Refining of Gold.—However won, the crude gold is run into ingots, and is usually refined at the mint, where it is coined. The gold obtained by chlorination contains 99·7 to 99·9 per cent. Au, but that from most other processes may be considerably less pure, containing silver as the chief impurity. As both gold and silver are not oxidised in air at any temperature, they are collected together by cupellation, and cannot be separated by continuing the process. Three methods are now used on a large scale for parting gold from silver—viz., the chlorine, sulphuric acid, and electrolytic processes.

1. **Removal of Silver as Chloride** (*Miller's Process*).—When chlorine is passed through fused gold the metal is unattacked because the temperature is above the decomposition temperature of gold chloride. Silver chloride on the contrary is stable at this temperature. These principles are applied by passing chlorine through a fireclay pipe to the bottom of the crucible containing the melted gold. A layer of fused silver chloride separates on the surface of the gold, and any antimony, arsenic,

lead or bismuth is volatilised as chloride. Formerly a similar effect, as far as removal of Sb, etc., is concerned, was obtained by throwing $HgCl_2$ upon the surface of the melted gold. If large quantities of base metals are present it is best to remove them partly, either by treatment with nitre, or by the method suggested by Rose, in which air or oxygen is blown through the molten metal covered with slag made by adding borax and sand to the crucible charge. The separated chloride carries from 5 to 10 per cent. of gold, for the recovery of which it is fused with soda carbonate. Metallic gold separates out, together with about an equal weight of silver, and is allowed to solidify when the fluid chlorides are poured off and cast into slabs. These slabs are boiled with water in flannel bags for some days to remove chlorides of the base metals, and the silver is afterwards reduced by electrolytic action by means of iron plates, fairly pure metallic silver, and chloride of iron being produced.

2. **Separation by Dissolution of the Silver in Acids ("Parting").**—Advantage can be taken of the solubility of silver in nitric acid and the insolubility of gold in the same menstruum for separating the metals, but the process is only efficient when the proportion of silver to gold is not less than 2 : 1, because otherwise the gold left on the surface of the alloy obstructs the action of the acid unduly. In order to ensure this proportion, the gold generally has to be fused with additional silver. The amount formerly used was sufficient to lower the proportion of gold to one-fourth of the whole, the process of separation being called on that account "quartation." The silver is recovered by precipitation as chloride. The process is now less practised than formerly because of the high price of nitric acid as compared with that of sulphuric acid. Parting by sulphuric acid has consequently displaced the nitric acid method. In this case the proportion of gold should not exceed one-half of the silver and more than one-tenth of copper is detrimental. The addition of some copper, however, is advantageous in promoting the dissolution of the silver. Gold bullion containing much base metal is first "toughened" by fusion with saltpetre. The granulated alloy is boiled with about two and a-half times its weight of strong sulphuric acid in a cast-iron retort. When the parting is complete (after three boilings) the liquid containing silver sulphate and copper sulphate is decanted, and the gold is washed and fused; the silver is recovered by precipitation with copper.

3. **The Electrolytic Refining Process** has made considerable progress in recent years, especially in America. The method used is a combination of two processes—the *Moebius* and the *Wohlwill* processes. The former has been described under silver

refining (p. 332). The anode mud from this process, containing gold. platinum, and lead, is melted down and used as the anodes in the Wohlwill process, in which the electrolyte is hydrochloric acid. Gold, copper, etc., are dissolved at the anodes, and pure gold is deposited at the cathodes, silver remaining undissolved. In American practice gelatine is added to the electrolyte in the Moebius process, and the silver deposited in a coherent instead of in a granular state. The electrolyte in the second stage (*i.e.*, the Wohlwill process) contains from 2 to 10 per cent. of hydrochloric acid, and from 2·5 to 6 per cent. of gold chloride, and is maintained at a temperature of 60° or 70° C. The cathodes are sheets of pure gold. Silver chloride is deposited as an anode mud, base metals are dissolved as chlorides, and accumulate in the solution, while practically pure gold is deposited on the cathodes. The electrolyte is renewed at intervals, and the gold remaining in it is precipitated by means of ferrous sulphate. Platinum, palladium, etc., are dissolved with the gold, but are not precipitated at the cathodes, and accumulate in the solution. They are afterwards precipitated by means of ammonium chloride The recovery of these metals constitutes an important advantage in the Wohlwill process.

Properties and Uses of Gold.—Gold melts at 1,064° C. = 1,948° F. Its specific gravity is 19·32 when cast, but can be raised to 19·65 by hammering. It is a most resistant metal, being very inactive chemically, on which account, as well as on account of its comparative rarity, it is suitable for coinage—its chief use. Unlike silver, it is untarnished by sulphur. An arbitrary method for computing the fineness of gold consists in stating the proportion of Au with reference to the standard 24 carats for pure gold. Thus, the sovereign, 22 carats fine, contains 91·66 per cent. of gold and 8·33 per cent. of alloying metal (in England copper, but in Australia silver). Most foreign coinage contains 90 per cent. of gold. The only alloys of gold of importance are those with copper and silver. Alloys containing iron are, however, used to some extent in jewellery in France; those containing 15 to 20 per cent. of iron are known as "*or gris*," and that with 25 per cent. of iron is "*or bleu*." The industrial uses of gold are limited by its high price. It withstands the action of sulphuric acid better than does platinum, and is, therefore, adopted for lining platinum vitriol stills. Being very malleable, it is used for making gold leaf for ornamental gilding. Gold-plating by the electrolysis of the double cyanide of gold and potassium is also largely practised.

PLATINUM AND ITS CONGENERS.

The metals platinum, palladium, rhodium, osmium, ruthenium, and iridium constitute what is known as the platinum group, and occur associated together in the native state in alluvial deposits—chiefly in the Ural district. The composition of native platinum may be gathered from the following analysis :—

	Per cent.
Platinum,	84·30
Rhodium,	3·46
Iridium,	1·46
Palladium,	1·06
Osmium,	1·03
Copper,	0·74
Iron,	5·31
Lime,	0·12
Quartz,	0·60

The ore is often associated with grains of a hard refractory alloy of osmium and iridium (**osmiridium**). The native grains of osmiridium are generally used for the points of pens. Unlike gold, platinum does not readily amalgamate with mercury, so that when gold accompanies the platinum sand it is first extracted by amalgamation.

Platinum has never been found other than native until recently, when a platinum arsenide, $PtAs_2$, **sperrylite,** has been found in the pyritic nickeliferous deposits of the Sudbury mines (see *Nickel*, p. 310).

Winning Platinum from its Ore.—The refractory character and high price of the metals of the platinum group make their winning and separation almost a laboratory operation. The opening up of the ore may be effected by wet or dry methods. By the former process the ore is heated to redness and digested with hydrochloric acid, which dissolves the base metals. It is then treated in retorts with aqua regia, by which palladium, rhodium, platinum, and a little iridium are dissolved; osmic acid passes over into the distillate, and osmiridium, ruthenium, chrome iron ore, and titanic iron ore remain undissolved. The solution containing the platinum is neutralised with sodium carbonate, and the palladium is precipitated from it by mercuric cyanide. The platinum, together with a little iridium, is then precipitated as the double chloride with ammonia, $(NH_4)_2PtCl_6$. When this precipitate is ignited, spongy platinum containing a little iridium is left, and is compressed and melted in a lime furnace heated by the oxyhydrogen jet. Instead of hydrogen, common coal gas is now usually employed. The lime of the furnace absorbs the slags of the oxides of iron and copper which

are formed during the operation. The platinum obtained in this manner is hardened by the presence of iridium, an advantage for some purposes.

A more modern process consists in heating platinum ore in a small reverberatory furnace, with galena and some glass. Litharge is then added, and the metallic lead formed by its reaction with the galena (p. 268) dissolves the platinum and its accompanying metals, allowing the osmiridium to sink to the bottom of the charge. The platiniferous lead is run off and cupelled, and the crude spongy platinum fused in an oxyhydrogen furnace, the high temperature of which volatilises any base metals present as impurities, as well as silver, gold, palladium, and osmium.

Preparation of Pure Platinum.—This is a matter of some difficulty. Matthey's process is as follows:—The granulated alloy of commercial platinum with six times its weight of pure lead is dissolved in dilute nitric acid. The solution contains most of the lead, copper, iron, palladium, and rhodium. The residue is digested with weak aqua regia, which dissolves platinum and lead, and leaves iridium unattacked. Lead is separated in the filtrate by means of sulphuric acid, and the platinum chloride dissolved in distilled water and treated with an excess of chloride of ammonium and sodium. The whole is heated to about 80° C. for some days, and a firm mass of ammonium platinochloride is obtained. This is washed with ammonium chloride and hydrochloric acid, mixed with potassium bisulphate and a small proportion of ammonium bisulphate, and gradually heated to dull redness. Platinum is thus reduced and rhodium remains as bisulphate of rhodium and potassium, which is extracted with boiling water. The spongy platinum thus obtained is very pure, and merely requires to be washed and melted.

The remaining platinum metals have but few industrial applications, and their extraction need not be described.

Properties and Uses of Platinum.—Platinum is a soft metal of great tenacity; it has a specific gravity of 21·5, and a fusing point of 1,730° C. Its chemical inertness makes it of use in the laboratory and chemical works for vessels exposed to strong acids—*e.g.*, vitriol stills. The fact that its coefficient of expansion is nearly identical with that of glass enables platinum wires to be sealed through glass apparatus, as in eudiometers and incandescent electric lamps. Platinum has now been replaced for this purpose, however, by "platinite," an alloy of iron and nickel (see p. 317). Platinum and platinum-rhodium (an alloy containing 10 per cent. of the latter metal) thermo-electric couples are used in pyrometry (p. 113). The resistance

of platinum to corrosion renders it and its iridium alloy (10 per cent. Ir) useful for standard weights and measures.

Platinum is very largely used (about one-third of the total consumption) in the dental industry, for the manufacture of pins for attaching artificial teeth to the plate, and for other purposes. There has also been a considerable increase in the use of platinum in jewellery; it is said to be the best material for mounting diamonds. The development of electrical technics entails a steadily growing consumption of platinum for anodes (*cf.* electrolytic alkali industry), and for electrically heated furnaces. By reduction of platinum salt solutions the metal is obtained as a very fine black powder ("platinum black"). In this state it has the property of accelerating chemical reactions among gases without itself being affected ("platinum catalysis"). The most important industrial use of platinum black is in the contact process for making sulphuric acid (see Vol. II.). Platinum salts—*e.g.*, platinocyanides and platinochlorides—also find technical utilisation in photography and the ceramic arts.

METALS DIFFICULT OF REDUCTION.

Metals, the oxides of which have high heats of combination, were naturally the last to be reduced in the laboratory, and yet later on an industrial scale. Such metals are manganese, aluminium, magnesium, and the metals of the alkalies and alkaline earths. They are probably all reducible by carbon if the temperature be high enough, but in some cases—*e.g.*, in the case of aluminium—this is so high that an electric furnace is the only means of attaining it, when it becomes difficult to assert that the effect is due to heat alone. The volatility of the metals of the alkalies, and their consequent removal from the sphere of reaction, assists the reducing action of the carbon, and enables them to be used in their turn as reducing agents in methods applied for the reduction of less volatile metals. Owing to the fact that electrical energy can be economically produced of any required voltage to correspond with the heat of combination of the intended electrolyte (p. 118), electrolysis often presents advantages in the reduction of metals of this class. Seeing that many of these metals have a higher heat of combination with oxygen than has hydrogen, it follows that the electrolysis of aqueous solutions is generally out of the question, because the water would be the compound chiefly decomposed, and the use of fused salts—*e.g.*, chlorides and fluorides—is, therefore, adopted instead.

The chemical energy represented by a metal of this class in the free state warrants the *prima facie* conclusion that it would be spontaneously reconverted into oxide on exposure to the atmosphere. This is true of some, notably sodium and potassium, but is not applicable to others—*e.g.*, magnesium and aluminium.

In these instances two causes may be stated for the inertness of the metal. The first and most important is that in a large number of cases of exothermic reactions the starting of the change needs the impress upon the reagents of a small initial charge of energy. This is only a particular case of what is generally true of the conversion of potential into kinetic energy, and chemically may be compared with the detonation of an explosive. Usually this initial change is brought about by raising the temperature of the metal, which is capable of vigorous oxidation—*e.g.*, the heating of magnesium wire previous to its deflagration. The second cause, though secondary in kind, may be of importance equal to the first. It is that the metal undergoes superficial oxidation, and when the oxide is unattacked by atmospheric agencies the coating first formed protects, in great measure, the metal beneath. This is well seen in the case of aluminium.

I. **ALUMINIUM.**—1. **Ores of Aluminium.**—**Corundum**, aluminium oxide, Al_2O_3. This mineral, which is a fairly pure form of crystalline alumina, occurs in India, Siberia, and the United States. It contains about 93 per cent. of Al_2O_3, and is characterised by its extreme hardness (exemplified by that of emery, an impure form of the same substance), on which account it is mainly used for abrading purposes. The sapphire and ruby are coloured varieties of the same mineral. Its comparative rarity and hardness make it unsuitable for use as a source of aluminium.

Bauxite, hydrated oxide of aluminium, $Al_2O_3 2H_2O$.—This form of oxide, which is rarely pure, is found in France and Ireland; it varies much in quality, containing

Al_2O_3, ...	30 to 60 per cent.
Fe_2O_3, ...	3 to 25 „

the remainder being chiefly silica, titanic acid, and water of hydration.

Cryolite, a double fluoride of aluminium and sodium, $Al_2F_6 . 6NaF$.—This occurs at Ivigtuk in Greenland as a white, crystalline, translucent mineral, which is readily fusible, and is used in the manufacture of aluminium.

Clay, which is essentially aluminium silicate, $Al_2O_3 . 2SiO_2$, $2H_2O$, and is formed by the disintegration of felspathic rocks,

is the most abundant aluminium mineral, but is not used as a source of the metal, owing to the difficulty of separating silica.

The chief ore of aluminium, bauxite, has to be treated for the production of pure alumina before the metal can be won: for this purpose it was formerly fused with sodium carbonate, sodium aluminate being formed and ferric oxide left unattacked. The mass was leached with water and the solution treated with CO_2, whereby alumina and sodium carbonate were produced. The method now used is to agitate the crushed and calcined ore with a solution of caustic soda of specific gravity 1·15 in a cylinder or keir heated by steam. After about three hours the solution is diluted to a specific gravity of about 1·25 and filtered. It has been found that a solution of sodium aluminate prepared in this way is sufficiently unstable to have its decomposition determined by the addition of a small quantity of alumina, the caustic soda liberated being incapable of redissolving alumina hydrated to the extent of that thus thrown down. Sodium silicate is not affected under these conditions (as it is by excess of CO_2), and contamination of the alumina with silica is therefore avoided. The decomposition is carried out in cylinders provided with agitators. In about 36 hours 70 per cent. of the alumina in solution is precipitated as hydroxide. The clear liquor is run off into weak liquor tanks, concentrated, and used again. The hydroxide is filter-pressed, washed free from soda, partially dried by means of compressed air, and finally calcined at a temperature of 1,000° C., when the alumina becomes crystalline and loses its power of absorbing water.

2. **Winning of Aluminium.**—Unlike the generality of metals, aluminium cannot be directly reduced by carbon at ordinary furnace temperatures, as the equation $Al_2O_3 + 3C = Al_2 + 3CO$ involves the absorption of 305 Cal. As aluminium alloys with most metals with evolution of heat, the reduction of it in this form—viz., as an alloy—can be attained with a smaller absorption of heat than when the metal itself is reduced, so that when alumina, carbon, and copper are heated to a very high temperature, as in an electric furnace, an aluminium-copper alloy results. An indirect chemical method or a direct application of electrical energy is consequently adopted for the commercial reduction of unalloyed aluminium.

(*a*) **Indirect Reduction by Chemical Means.**—Although no compound of aluminium can be directly reduced by means of carbon, yet one of its most refractory compounds, the oxide, having the high heat of combination of 392 Cal., can be converted into the chloride (heat of combination 322 Cal.), and this reduced to metal by the action of sodium, itself won by carbon. The

process, due to Deville, is now obsolete; it consists in heating a mixture of alumina and carbon in a stream of chlorine, the following reaction occurring :—

$$Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO.$$

The carbon is necessary for supplying, by its union with O, the energy represented by the difference in the formation heats of Al_2O_3 and Al_2Cl_6.

Although aluminium chloride can be obtained by dissolving alumina in hydrochloric acid, it is then an hydrated salt, which is decomposed into alumina and hydrochloric acid when heated. The method given above, or one equivalent thereto, is, therefore, essential for the preparation of anhydrous Al_2Cl_6. By using a mixture of alumina and salt instead of alumina, the double chloride of aluminium and sodium, $Al_2Cl_6 . 6NaCl$, is obtained, and is a more convenient form for the subsequent reduction to aluminium. The second stage of the reaction consists in heating this double chloride with sodium :—

$$Al_2Cl_6 . 6NaCl + Na_6 = Al_2 + 12NaCl.$$

A modification of this process consists in the use of cryolite or of aluminium fluoride in place of the double chloride of aluminium and sodium, sodium still being the reducing agent.

(*b*) **Reduction of Aluminium by Electrolysis.**—When aluminium salts are electrolysed in aqueous solution, they do not yield the metal, hydrogen being reduced in preference to aluminium. Fused salts, such as the double chloride of aluminium and sodium, are, therefore, used. To avoid the cost of a bath of a pure halogen salt of aluminium, needing constant renewal, alumina itself (prepared in the manner described above) is fed into a bath of fused cryolite, in which case the alumina is dissolved and is decomposed by the current in place of the halogen salt.

The process is carried out in an iron vessel, A (Fig. 53), lined with carbon, serving to contain the electrolyte, B, and to act as the cathode, the current entering by the copper pins, D. Passing through the graphite covers, F, is a bundle of carbon rods, C, immersed in the bath, which is maintained in fusion by the heat generated by the passage of the current; this bundle of rods constitutes the anode and is consumed by the oxygen resulting from the electrolysis of the alumina, fed regularly to the bath during the process. A taphole, E, at the bottom of the vessel containing the electrolyte serves for the collection of the separated aluminium. The electrical pressure requisite is 5 to 6 volts., the output, of course, depending on the number of amperes supplied at this pressure. The process was worked out independently by

Hall in America, and by Héroult in France, but, as now operated, the processes are practically identical. and at the present time the whole of the world's output of aluminium is produced either by the Hall or by the Héroult process. The process is conducted where cheap power—*e.g.*, from a waterfall—is obtainable. The substitution of aluminium sulphide dissolved in a bath of fused alkaline chloride for aluminium oxide dissolved in a fluoride has been devised, and it presents the advantages that the anode is not consumed—as sulphur is liberated there instead of oxygen, and the temperature is too low for the production of CS_2,—and that a lower voltage—*e.g.*, 3 volts—is required. The method has not been found successful in practice.

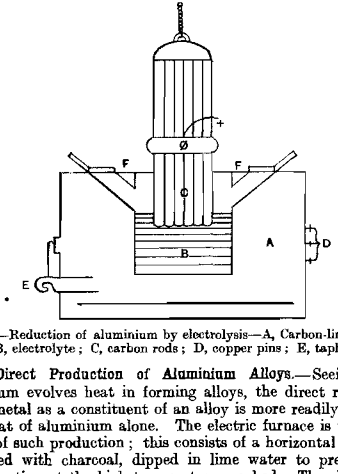


Fig. 53.—Reduction of aluminium by electrolysis—A, Carbon-lined vessel; B, electrolyte; C, carbon rods; D, copper pins; E, taphole.

(c) Direct Production of Aluminium Alloys.—Seeing that aluminium evolves heat in forming alloys, the direct reduction of the metal as a constituent of an alloy is more readily effected than that of aluminium alone. The electric furnace is the chief means of such production; this consists of a horizontal firebrick box lined with charcoal, dipped in lime water to prevent its agglomeration at the high temperature reached. The electrodes project horizontally into the furnace at each end and are heavy carbon rods, which can be fed into the furnace as they are consumed. The charge, consisting of alumina, carbon, and copper, is placed between the electrodes and fused by the heat resulting

from the electrical energy supplied, the conversion of which into heat is due to the resistance of the charge. A furnace of industrial size will take about 125 horse-power and an alloy of copper and aluminium, containing 15 to 35 per cent. Al, is obtained. The following is a typical product :—

	Per cent.
Copper,	71·5
Aluminium,	20·1
Silicon,	4·1
Iron,	4·2

In more modern practice the disposition of the furnace is vertical, the carbon lining serving as the lower electrode, the arrangement being somewhat similar to that adopted in the electrolytic process (*v.s.*).

The same process can be adopted for preparing other aluminium alloys—*e.g.*, ferro-aluminium.

The impurities commonly met with in commercial aluminium are *silicon*, iron, and sodium. *Silicon* renders aluminium brittle, and also impairs its resistance to corrosion. In high-grade material its percentage should not exceed 0·3 per cent. Iron occurs to the extent of 0·2 to 0·3 per cent., and also impairs the ductility and non-corroding properties of aluminium. Sodium is more injurious than either of the above impurities, but is rarely found except in traces.

3. **Properties and Uses of Aluminium.**—*Aluminium* is a white metal of specific gravity ranging from 2·52 to 2·76, according to its method of treatment, and melting point 657° C. (= 1,215° F.). Although having a high heat of combination with oxygen, it is not readily corroded in air, in the massive state; when finely divided, however, by amalgamation with mercury or alloying with antimony, it oxidises readily. Its inertness when massive is largely due to the protection afforded it by the first film of oxide resulting from its corrosion. When pure (free from silicon and iron) it can be used for cooking vessels and brought freely into contact with food and drink without being attacked to an injurious extent. It is largely used for military fittings on account of its lightness. For a similar reason (and for its silvery appearance), it is used as an industrial metal for smallware and structures where lightness and resistance to corrosion are required, all kinds of small articles for daily use being made in large quantities. Pure *aluminium* has a *tensile strength*, when *cast*, of about 5 tons per square inch, and when wrought, of 12 to 16 (see p. 27).

Its alloys are more useful than the pure metal. Two classes may be distinguished :—(1) Those consisting of 90 per

cent. or more Al, the remainder being some foreign metal added to increase the strength of the material without greatly raising its specific gravity. Thus, an alloy containing Al 94 Cu 6, has a specific gravity of 2·82 and a tensile strength of 24·7 tons; one with 2 to 3 per cent. of Ti has a tensile strength of 18 to 26 tons. Similar alloys have been prepared with tin, nickel, zinc, and silver respectively. *Magnalium* is an alloy of aluminium and magnesium, containing from 2 to 10 per cent. of the latter element. It is appreciably lighter than aluminium. It works well in the lathe, makes good castings, and does not easily tarnish. It is, therefore, suitable for a variety of purposes. Compounds of aluminium and magnesium corresponding to the following formulæ have been isolated by chemical means:—AlMg, $AlMg_2$, Al_4Mg. Alloys of aluminium and zinc are now largely used in the automobile industry. Those containing up to 15 per cent. Zn are soft enough to be rolled or drawn, while beyond this amount the alloys are hard and more suitable for castings, as they are easily worked. *Ziskon* and *Zisium* are two of these alloys which have been introduced by Zeiss of Jena. The former has a specific gravity of 3·4, and is used where strength and lightness are required; the latter (sp. gr. 2·95) is used where ductility rather than strength is desirable. These aluminium-zinc alloys consist of single homogeneous solid solutions. Aluminium-copper alloys containing 3 to 5 per cent. of copper are sometimes used in the automobile industry. They give rise to a eutectic consisting of aluminium and the compound Al_2Cu. *Partinium* is an alloy containing Al 88·5 per cent., Cu 7·4 per cent., Zn 1·7 per cent., Si 1·1 per cent., and Fe 1·3 per cent. Alloys of aluminium and manganese containing 2 to 3 per cent. of manganese have also been used recently. Numerous other alloys have been introduced. *Heussler's alloy* contains aluminium, copper, and manganese, and is distinctly magnetic. *McAdamite* contains aluminium, zinc, and copper, while *Zimalium* is aluminium containing small quantities of manganese and zinc.

(2) The other class consists of aluminium bronzes and brasses. They are of the same class as ordinary copper alloys, but improved by the addition of aluminium. Thus, *aluminium bronze*, Cu 90, Al 10 per cent., may have a tensile strength of 40 tons; *aluminium brass*, Cu 63, Al 3·3, Zn 33·3 per cent., has a strength, when cast, of 20 tons. Such alloys are not only stronger but less easily corroded than ordinary brasses or bronzes (see *Copper alloys*, p. 266).

Aluminium is also used in casting steel, its effect being to reduce the oxides present and to decompose entangled CO; the quantity used is from 4 to 10 ozs. per ton, and may be applied

either as the metal itself or as ferro-aluminium containing 10 to 20 per cent. Al. Vast quantities of aluminium are now employed as a reducing agent for this and similar purposes. It is especially useful for reducing refractory oxides, such as that of chromium (see *Goldschmidt process*, p. 172). Its heat of reaction with iron oxide is utilised in the "Thermite" process (see p. 42). "Nickel Thermit" and "Titanium Thermite" are new applications of this principle, and are used for introducing these elements into molten cast iron. A further application is in the new explosive "*ammonal*," in which its great heat of oxidation is made use of to raise the gaseous products of the decomposition of ammonium nitrate to a very high temperature. Aluminium is now replacing magnesium in the manufacture of fireworks. It is also used for adding to zinc in zincing (p. 30) to hinder oxidation of the bath, and in the Parkes process (see *Lead*, p. 281).

A great hindrance to the extended application of aluminium has hitherto been the difficulty of soldering it successfully, but this is now overcome partly by the use of solder containing aluminium and the abandonment of such fluxes as are used for ordinary soldering; but more especially by the introduction of a process of autogenous welding. For this purpose portable oxy-acetylene blowpipe equipments are employed. The principal difficulty to be encountered is the formation of a film of oxide, which prevents the two surfaces uniting properly. This may be removed either by the application of pressure or by the use of special fluxes which dissolve the oxide. The refractory character of the oxide, the ease with which the metal is attacked by both acid and alkaline fluxes, and the high specific heat (0·25), no doubt account for this difficulty of soldering.

Aluminium is a good conductor of both heat and electricity, its electrical conductivity being about 60 per cent. of that of electrolytic copper. As a material for electrical conductors, therefore, it has a large field of usefulness, the difficulties at first met with in regard to jointing, etc., having now been overcome. There is an actual saving in weight for equal conductivity if aluminium is used instead of copper.

Other important applications of aluminium include its use as a substitute for stone in lithographic work, and for the manufacture of metallic paints. The French Government proposes to replace the 5 and 10 centime copper pieces by aluminium coins.

II. **MAGNESIUM.**—1. **Sources of Magnesium.**—Magnesium is widely distributed in the form of earthy rocks, such as *magnesite*, $MgCO_3$, *dolomite*, $MgCO_3 . CaCO_3$, and silicates—*e.g.*, *asbestos* and *serpentine*. But none of these is directly available

for winning the metal. Large deposits of magnesium salts, such as *kieserite*, $MgSO_4 . H_2O$, *carnallite*, $MgCl_2 . KCl . 6H_2O$, and *kainite*, $K_2SO_4 . MgSO_4 . MgCl_2 . 6H_2O$, occur in Stassfurt, which can be worked up to yield a pure magnesium salt suitable for the obtainment of the metal.

2. **Winning of Magnesium.**—Sodium is used as a reducing agent to obtain magnesium from its chloride, in a manner similar to that of the old Deville process for making aluminium (p. 350). The fact that magnesium chloride is more stable than aluminium chloride, enables the former to be obtained anhydrous, mixed with potassium chloride, by heating carnallite. When the double chloride of magnesium and ammonium is substituted for carnallite, $MgCl_2$ itself can be obtained anhydrous, the ammonium chloride being volatilised. Ten parts of the dried carnallite are mixed with one of sodium and one of powdered fluor spar; the mixture is thrown into a red-hot crucible and covered until the main reaction is complete, when magnesium amounting to about three-quarters of the theoretical yield is obtained as a button. The crude metal, which contains silicon, may be purified by distillation, its volatility being similar to that of zinc (B.P. about 1,100° C. = 2,012° F.).

Magnesium is now mainly manufactured by the electrolysis of fused carnallite, the operation being carried out in an iron crucible, which serves as the cathode, a carbon rod constituting the anode. The carnallite is kept fused by heat externally applied. An indifferent or reducing atmosphere is maintained in the crucible to prevent oxidation of the magnesium, and the anode is surrounded by a fireclay tube through which the chlorine produced by the electrolysis is drawn off.

In the method employed by the Virginia Electrolytic Company at Holcomb's Rock, Va., a mixture of magnesium fluoride with the chloride of calcium or some other alkaline earth metal more electro-positive than magnesium is heated in order to render it anhydrous, a small percentage of an alkali fluoride being added as a flux. After the magnesium has been separated electrolytically hydrated magnesium chloride is added, and the whole subjected to a further dehydration, the resulting mixture of magnesium fluoride and calcium chloride being utilised in a second electrolysis. Haag has designed a cell divided into three sections. In the upper one carnallite is fused by resistance heating. In the central chamber electrolysis takes place, chlorine passing out through the hollow, perforated carbon anodes. The third chamber receives the molten magnesium and undecomposed carnallite, which are separated by an ingenious device. All the materials are kept molten by internal heating; liquid seals are

employed to prevent leakage, and radiation is prevented as far as possible by enclosing the cell in an outer chamber.

3. **Properties and Uses of Magnesium.**—*Magnesium is a white* metal of specific gravity 1·74 and melting point 750° C. = 1,382° F.; it is easily corroded in a moist atmosphere, becoming covered with a white coating of hydrated oxide. It is malleable, and when hot—*e.g.*, at 450° C. = 842° F.—can be drawn into wire and flattened into ribbon. It is largely used in pyrotechny, both as ribbon and powder, and for producing a flash light for signalling and for photographic purposes. Thus its chief value arises from the ease with which it burns in air and the brilliant actinic light which it emits. The product of its combustion in air contains Mg_3N_2 as well as MgO. It is slowly attacked by water, especially when hot, and readily by dilute acids.

The pure metal has a tensile strength of about 14·5 tons per square inch, and a compressive strength of about 17 tons. It is employed in the laboratory as a reducing agent, especially in place of zinc, as it is free from arsenic.

Magnesium is employed to some extent as a deoxidiser in brass manufacture, an addition of 0·05 per cent. being usually sufficient for this purpose. It possesses an advantage over phosphorus in that an excess may be used without harm. It is also added to nickel to cause it to cast well. For use as a deoxidiser and in pyrotechny, however, maguesium is now being displaced by aluminium. Almost the only other use of magnesium is in the manufacture of magnalium alloys (see under *Aluminium*, p. 353).

III. **CALCIUM.—Sources of Calcium.**—This element is very *widely distributed in nature, especially as the carbonate which* exists in various forms—*e.g.*, calc-spar, chalk, marble, limestone, coral, etc.—numerous complex carbonates also occur—*e.g.*, dolomite, $CaCO_3 . MgCO_3$. Large quantities of the sulphate are also found as anhydrite, $CaSO_4$, and gypsum, $CaSO_4 . 2H_2O$. Other complex minerals contain calcium as silicate, phosphate, and borate.

Winning of Calcium.—Within the last few years metallic calcium has become a commercial product, and it is now manufactured in France, Germany, and America by the electrolysis of its fused salts.

The method employed by the Virginia Electrolytic Company may be described as a typical process for the electrolytic production of metals which are lighter than their molten electrolytes, and whose melting points are either higher or not much lower than the melting points of their electrolytes.

The cell is formed by a vessel, A, of cast iron and of circular form. The cathode B projects centrally through the bottom,

while a graphite ring, C, forms the anode, the electrodes being insulated from the iron vessel by the insulating compound *a*. The bottom of the vessel is protected by a chilled layer of the electrolyte produced by the water jacket D. The calcium set free collects within the water-cooled ring E, and is thus isolated from the gases which separate at the anode. The block of metal, *h*, which forms inside the ring is slowly raised out of the electrolyte

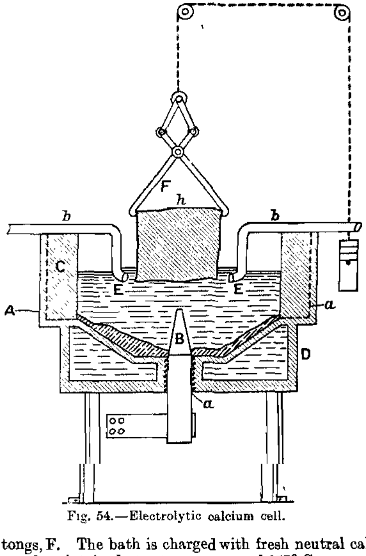


Fig. 54.—Electrolytic calcium cell.

by the tongs, F. The bath is charged with fresh neutral calcium chloride, and maintained at a temperature of 675° C.

Properties and Uses of Calcium.—The metal is sold in the form of grey sticks containing 96 to 98 per cent. of calcium. It oxidises slowly in dry air, but more quickly in air saturated with moisture. It is very light (sp. gr. 1.72), fairly

malleable, has a high specific heat, and is a good conductor of electricity. It is about as hard as aluminium, but at 400° C. becomes as soft as lead. It melts at about 800° C., and can be sublimed *in vacuo* between 700° and 800°. Its most interesting combinations are with hydrogen and nitrogen, forming the hydride, CaH_2, and the nitride, Ca_3N_2. The former reacts with water much like calcium carbide, and yields pure hydrogen. Under the name of "Hydrolithe" it is already employed to some extent for inflating balloons. The avidity of calcium for nitrogen will probably be made use of by metallurgists for eliminating this gas from iron, etc. As might be expected, calcium is also a powerful reducing agent, and these properties give it a promising field of usefulness in the refining of metals.

IV. **MANGANESE.**—1. **Ores of Manganese.**—Manganese is found chiefly as the dioxide MnO_2, both anhydrous as *pyrolusite* and *polianite*, and hydrated as *wad* and *psilomelane*; this last mineral also contains barium. Another oxide, Mn_2O_3, is found anhydrous, together with some silica, as *braunite*, and in the hydrated form as *manganite*. *Hausmannite* (Mn_3O_4) contains still less oxygen. The carbonate (*rhodochrosite*), silicate (*rhodonite*), and sulphide are also found. The following countries are the most important producers of manganese ore:—Russia, India, Brazil, Germany, and the United States.

2. **Winning of Manganese.**—Manganese can be reduced from its oxide by carbon at a high temperature; the metal thus obtained contains carbon. Moissan prepared manganese in this way in the electric furnace, and showed that by using excess of oxide the reduced metal may be obtained free from carbon and silicon. The method was put into commercial use, but the efficiency of the process was not such as to yield the metal at a low cost, partly because of the high volatility of manganese. It is more readily prepared, however, by reducing $MnCl_2$ by sodium or magnesium. In the latter case the dried powdered chloride, mixed with twice its weight of KCl, is fused and magnesium introduced in successive portions until an amount of this metal, equal to one-sixth of the weight of the manganese chloride, has been used.

A considerable amount of manganese is now made by the Goldschmidt aluminium reduction process (p. 172). The product may attain a high degree of purity, containing as much as 98 to 99 per cent. manganese. Lebau has shown, however, that the metal so produced may contain as much as 5 per cent. of silicon.

Manganese is not produced on a large scale save as *spiegeleisen* and *ferro-manganese*, which are obtained by reducing iron ores rich in manganese in a blast furnace. Both are used in

steel making (*q.v.*). *Silico-spiegel* is an alloy of iron and manganese in which these metals occur as silicides, and is also used in steel manufacture (see p. 191). Various other methods have been suggested for making ferro-manganese alloys. Of these, the *Simon process* is noteworthy, and was successfully applied for some time in France. It consisted in the electrolysis of a mass of fused calcium fluoride, in which oxide of manganese had been previously dissolved. In this respect it bears a resemblance to the aluminium extraction processes of Héroult and Hall. Greene and Wahl have suggested the reduction of pyrolusite by means of ferro-silicon in a basic-lined furnace. By this process an alloy containing 70 per cent. of iron, 29 per cent. of manganese, and as little as 0·7 per cent. of carbon was obtained. The method, however, has not been adopted on a commercial scale.* Various attempts have been made to prepare carbon-free ferro-manganese on a large scale, more particularly in the electric furnace. The problem appears to be a very difficult one, however, on account of the volatility of manganese and its tendency to form a very stable carbide, Mn_3C. The blast furnace, which has been so effectively attacked by the electric furnace as far as other ferro-alloys are concerned, still reigns supreme in the field of ferro-manganese, on account of the more economic production possible. The problem appears to be most likely to be solved by means of some of the newer forms of electric furnace described in the section on the "Electro-metallurgy of Iron and Steel" (p. 237).

An "*Electro-silico-spiegel*" is made in the Keller electric furnace by heating a mixture of ferro-silicon, flint, carbon, and manganese ore to a moderate temperature, care being taken to avoid volatilisation of manganese. The product contains 22 to 24 per cent. silicon, 38 to 40 per cent. manganese, and is thus double the strength of ordinary silico-spiegel. It is finding extensive use in steel works.

Manganese-copper can be produced by heating together copper, oxide of manganese, and carbon, and is used in copper refining to reduce over-oxidised copper in a manner analogous with the use of ferro-manganese in steel making.

3. **Properties and Uses of Manganese.**—It is a greyish-white metal of specific gravity 8·0, readily oxidised by moist air. It fuses at 1,245° C. It decomposes water at the boiling point. In addition to its use in steel making, manganese is used in the manufacture of bronze (see p. 266). Permanganates find use as disinfectants, manganese borate as a drier in paints and varnishes, and other compounds are used in the ceramic arts. Alloys of

* Ferro-silicon can also be used for reducing NiO, Cr_2O_3, and WO_3.

manganese with aluminium, antimony, tin, bismuth, arsenic, and boron are receiving much attention, owing to their remarkable magnetic properties (see *Heussler's alloy*, p. 353).

V. **CHROMIUM.**—The only chromium ore of commercial importance is *chromite* or *chrome-iron ore*, $FeO . Cr_2O_3$: it always contains alumina and magnesia. It is found in California, Canada, Rhodesia, and Asiatic Turkey. The metal is prepared in the electric furnace by Moissan's method, first as the carbide and then as the pure metal. The production of "cast chromium," corresponding with cast iron, containing about 10 per cent. of carbon, can be effected by heating a mixture of Cr_2O_3 and carbon in the electric furnace. The metal is refined by fusing it with lime in a furnace lined with calcium chromite. In this way practically pure chromium is obtained. An alternative method of preparing chromium is by reduction with aluminium. Chromic oxide is mixed with aluminium powder, and is fired by a fuse of mixed aluminium powder and barium peroxide, in which a strip of magnesium is embedded. The heat of the reaction is sufficient to fuse the resulting chromium into an ingot.

Properties and Uses of Chromium.—The metal has a brilliant grey colour, and, though hard, can be polished without difficulty. It has a specific gravity of 6·92, and its melting point is higher than that of platinum. It is non-magnetic, keeps its polish in air, and is not readily attacked by acids. Chromium and its compounds are used metallurgically in the manufacture of alloys and of furnace linings, and chemically as a constituent in colouring materials, mordants, oxidising agents, and tannages. Ferrochrome is the form in which chromium is introduced into steel (see under *Iron and Steel*). It is made both in the blast furnace and in the electric furnace. Blast-furnace alloys contain 12 to 40 per cent. Cr, 1·5 to 2·5 per cent. Mn, and 5 to 7 per cent. C. Electric-furnace alloys contain about 6·5 per cent. Cr and 5 to 10 per cent. C. Refined alloys low in carbon are also made in special furnaces (see under *Ferro-alloys*, p. 237). Chromite brick for furnace linings is generally made of crude chromite and tar, but sometimes of a mixture of chromite with kaolin, bauxite, lime, or some other material. For chrome pigments and mordants, see Vol. II.

VI. **MOLYBDENUM.**—Two minerals are used commercially as the source of the metal—viz., *molybdenite*, the sulphide MoS_2, and *wulfenite*, which is essentially lead molybdate, $PbMoO_4$. The metal can be prepared in a manner similar to that used for chromium. It may be obtained free from carbon by heating a mixture of the dioxide MoO_2 with defect of carbon in the electric

furnace. It is white, has a specific gravity of 9·0, is as malleable as iron, and can be filed and forged. It is only slightly oxidised in air. When heated with carbon it absorbs a small percentage of that substance, and can then be hardened by quenching in the manner characteristic of steel. It is used to a small extent in making special steels. Ferro-molybdenum is made in the same way as ferro-tungsten, which it resembles, and contains 50 to 85 per cent. of molybdenum and 0·4 to 2 or more per cent. of carbon. A large amount of ammonium molybdate is used in the laboratory in the estimation of phosphorus; it is also used as a fireproofing material, and as a germicide. Sodium molybdate is used to give a blue colour in making pottery, and in dyeing silk, wool, and leather.

VII. **TUNGSTEN.—Ores of Tungsten.**—The tungsten minerals used as ores are *hubnerite*, a tungstate of manganese; *wolframite*, a tungstate of iron and manganese; *ferberite*, a tungstate of iron; and *scheelite*, a tungstate of calcium. The first three minerals grade into each other, and are sometimes classed together as wolframite. They are usually found in granite countries, and are sometimes mixed with tinstone (see under *Tin*). Tungsten ores occur in Cornwall, Queensland, the Malay States, Rhodesia, Spain, Portugal, and the United States.

Winning of Tungsten.—The method of extracting tungsten from its ores is both lengthy and complicated. Sodium tungstate is first formed by heating the finely-ground ore with sodium carbonate in a reverberatory furnace. The melt is extracted with boiling water, and filtered from the insoluble residue containing FeO, MnO, SnO_2, etc. If the furnacing has been carried out correctly no tin goes into solution. Yellow tungstic acid is then precipitated from the solution by means of hydrochloric acid, filtered, and dried. The tungstic acid (WO_3) is finally reduced by heating with carbon in crucibles in the electric furnace. When the carbon is used in defect, and the mass is not completely fused, the pure metal results. If excess of carbon be employed this is absorbed by the metal probably as a definite carbide W_2C. As in the case of chromium, there is a rival method for the manufacture of tungsten—viz., the reduction of tungstic acid by aluminium (*Goldschmidt process*).

Properties and Uses of Tungsten.—The physical properties of tungsten depend on the manner of its preparation. It is difficultly fusible, its melting point having been recently given as 2,800° to 3,000° C. = 5,072° to 5,432° F. When free from carbon it can be drilled and filed easily, and is not magnetic. Pure tungsten, melted in the electric furnace, has a specific gravity of 18·7. The metal is attacked by fluorine at ordinary

temperatures, and by the other halogens at higher temperatures. At bright redness it burns in air and decomposes water vapour. The metal is attacked slowly by strong mineral acids, and rapidly by fused oxidising agents. The most important use of tungsten is in the manufacture of tool steel (see p. 222). For this purpose it is employed either as a powder or as ferro-tungsten. The latter alloy is usually made by melting together Swedish iron, charcoal, and tungsten powder in the electric furnace. Three grades are manufactured commercially, containing about (1) 65 per cent. tungsten and 1·5 per cent. carbon, (2) 80 per cent. tungsten and 1·5 per cent. carbon, (3) nearly 90 per cent. tungsten and about 0·4 per cent. carbon. Smaller quantities of silicon, manganese, phosphorus, and sulphur are also present. The high melting point of tungsten makes it available for use as a filament in incandescent electric lamps. The so-called Osram lamp has a filament of practically pure tungsten. For this purpose the powdered metal is made into a paste with an organic binding agent, such as gum arabic, and squirted into threads. These are then subjected to various processes, by means of which all carbon is said to be removed, leaving the metal practically pure. Tungsten is used in the manufacture of small crucibles for use in the electric furnace, the method of manufacture being similar to that employed for filaments. Large quantities of sodium tungstate are also used as a fireproofing material.

VIII. **VANADIUM.—Ores of Vanadium.**—The most important source of vanadium appears to be the mines in Peru, where a vanadium-bearing asphaltite ("patronite") occurs, containing about 40 per cent. of vanadium sulphide. Important vanadium deposits are also found in Colorado, where it occurs as *roscoelite*, a green vanadium mica, and *carnotite*, K_2O, $2U_2O_3$, V_2O_5, $3H_2O$. Lead vanadate also occurs naturally associated with other minerals in Central America, Spain, and Cheshire.

Winning of Vanadium.—The roscoelite ores of Colorado are worked up as follows:—The finely-crushed ore is roasted with salt and leached with water, whereby a solution containing sodium vanadate, and possibly some vanadium chloride, is obtained. This is then treated with ferrous sulphate, and the precipitated ferric vanadate is filtered, dried, and sold as a dark olive-green powder containing 34 per cent. of vanadium. The *Haynes process* for treating carnotite ore consists in agitating the crushed ore in a revolving barrel with a boiling solution of sodium carbonate. Sodium uranate is precipitated from the filtered solution by means of caustic soda, and forms the uranium product. From the filtrate calcium vanadate is precipitated by means of slaked lime, and this forms the vanadium product. The

final liquors contain caustic soda, and are recarbonated by means of furnace gases. The vanadium products thus obtained are sold for conversion into ferro-vanadium.

Uses of Vanadium.—The metal itself has little commercial importance. It has been prepared by reducing vanadic acid with aluminium in magnesia-lined crucibles, and by other means. It is a hard, steel-grey, brittle metal. Its most important use *is as ferro-vanadium in the manufacture of vanadium steel.* The alloy is made by reducing vanadic acid in presence of iron and charcoal in an electric furnace (see under *Steel*, p. 237). Vanadium compounds are used as mordants in printing and dyeing. The anhydride, V_2O_5, also greatly accelerates certain oxidation processes, such as the action of nitric acid on sugar, and the oxidation of alcohol. It has also been used in place of platinum as a catalyst in the contact process of making sulphuric acid.

IX. **TANTALUM.—Ores of Tantalum.**—The most common ores of tantalum are *tantalite* and *columbite.* These minerals consist essentially of tantalates and columbates (niobates) of iron and manganese, and occur principally in Australia and the United States. *Fergusonite* and *samarskite* are also fairly common, and contain columbates and tantalates of iron, calcium, yttrium, and cerium. Samarskite also contains uranium oxide.

Metallurgy of Tantalum.—Berzelius obtained the metal by converting the ore into alkaline fluotantalates and reducing with potassium or sodium. Modern commercial processes for preparing the metal are proprietary, and the published accounts of them are obscure. Bolton purifies the crude metal by heating *in vacuo* in an electric furnace. The British Thomson-Houston Company electrolyses a fused salt of the metal between an anode of impure tantalum and a cathode of the pure metal. Another refining process due to von Piriani takes advantage of the fact that tantalum has a great affinity for hydrogen. A mixture of tantalum chloride vapour and hydrogen is heated, yielding a very brittle metallic mass containing a large amount of occluded hydrogen. This is then strongly heated *in vacuo* in such a manner as to allow the liberated hydrogen to be constantly withdrawn.

For further details, the reader is referred to the *Mineral Industry*, 1908, p. 802; and the *Journ. Chem. Soc.*, 1905, A. ii., 259.

Properties and Uses of Tantalum.—The pure metal has a specific gravity of 16·5, and melts at about 2,200° C. = 3,992° F. A wire heated by an electric current contracts by 7·8 per cent. of its length in twelve hours, and becomes correspondingly more dense. The metal has the unusual characteristic of becoming softer under hammering. Carbon up to 1 per cent. softens tantalum without increasing its ductility; above that amount it

makes the metal brittle. In chemical properties tantalum resembles gold and platinum. It is not affected, however, by aqua regia, but is attacked by fused alkalies and by hydrofluoric acid. The metal forms no alloys of commercial importance, but it is now being largely used in making filaments for incandescent electric lamps. This is the only practical use to which tantalum has, so far, been put.

X. **SODIUM.**—Sodium compounds are so abundant as to need little mention. The most important found naturally are common salt, $NaCl$, Chili saltpetre, $NaNO_3$, cryolite, $3NaF . AlF_3$, the carbonate, Na_2CO_3, and sulphate, Na_2SO_4 (*Thénardite*). Formerly, sodium was obtained by reducing the carbonate with carbon—

$$Na_2CO_3 + C_2 = Na_2 + 3CO.$$

The reaction is endothermic, according to data determined at the ordinary temperature, 186 Cal. being absorbed; the volatility of sodium no doubt assists the occurrence of the reaction, the product, Na, being spontaneously removed from the sphere of action by distillation. The operation was effected by heating a mixture of 30 parts of sodium carbonate, 13 of charcoal, and 5 of calcium carbonate in a horizontal iron tube connected with an iron condenser opening into a receiver containing mineral oil; a temperature of about 1,500° C. = 2,732° F. was requisite for the distillation. The calcium carbonate was added to prevent the sodium carbonate from flowing away from the charcoal when fused.

More recently sodium was made by Castner's process, which consists in heating caustic soda with one-fifth its weight of "carbide of iron," a substance made by heating iron oxide with tar; the function of the iron in this mixture is to keep the carbon immersed in the fused caustic soda. The reduction of the sodium is said to take place according to the equation—

$$4NaOH + C_2 = Na_2CO_3 + Na_2 + 2H_2 + CO.$$

This reaction is endothermic, requiring the absorption of 106 Cal., considerably less than in the case of the older process. The operation was carried out in steel crucibles set in a furnace heated by producer gas, a temperature of about 800° C. = 1,472° F. being requisite. The crucibles were covered with domes carrying an exit pipe, through which the sodium distilled into a receiver containing mineral oil. A yield of about 90 per cent. was obtained. The sodium carbonate obtained as a bye-product was leached out of the spent contents of the crucible, causticised, and used again.

Electrolytic Process.—All purely chemical methods for the manufacture of sodium are obsolete, the metal being produced

exclusively by electrolysis. The process mostly used is one devised by Castner, the inventor of the chemical method described above. The apparatus used is shown diagrammatically in the figure. A is a cylindrical steel crucible with an opening at the bottom, through which the iron cathode B passes. The crucible is set in a flue, so that the body of it is heated while the neck C remains cool. The caustic soda which fills the crucible consequently solidifies in the neck C, and protects the joint made between the cathode and the crucible. The anode D, which may be a cylinder with vertical slits to allow free flow of the electrolyte, surrounds the upper part of the cathode. This upper part is encircled by a cylinder of wire gauze E depending from the

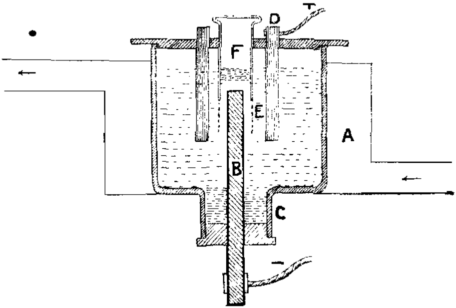


Fig. 55.

collecting pot F. As electrolysis proceeds, fused sodium floats from the cathode and collects on the surface of the fused caustic soda in the pot F. Hydrogen is also liberated at the cathode and oxygen at the anode, both gases escaping through the loosely fitting top. The sodium is hindered from straying into the anode compartment by the wire gauze, through which it cannot easily pass on account of its high surface tension. The temperature of the electrolyte is not allowed to rise above 330° C., or 20° above the melting point of caustic soda. Castner states that even at its melting point caustic soda dissolves both sodium and oxygen, and that this dissolution becomes rapidly greater with rise of temperature until a point is reached at which substantially no

permanent separation of the products of electrolysis can be secured. If the temperature is too low the hydrate is not sufficiently fused, and ceases to act as an electrolyte. The extreme fluidity of caustic soda, and the ease with which it wets all surfaces allow that body, on the other hand, to pass freely through the gauze. The molten sodium is removed by means of a large perforated spoon, cast into brick form, trimmed to remove adherent oxide, and immersed in paraffin oil.

In some works electrodes of copper and nickel are employed. Various modifications of the above process are also in use. A cell devised by *Rathenau* and *Suter* is used at Bitterfeld (Germany) in which the cathodes are only allowed to touch the surface of the electrolyte and the gauze diaphragm is dispensed with. The metallic sodium gathers in globules at the point where the cathodes touch the electrolyte, and is collected in a perforated ladle at very short intervals. The *Becker process* used in France differs from the Castner in that the electrolyte consists of a mixture of sodium carbonate and hydroxide.

A process has been devised by *Darling* in which sodium nitrate is fused by external heat and electrolysed between iron electrodes. To separate the sodium from the oxides of nitrogen evolved at the anode a partition was employed consisting of magnesia packed between two perforated steel cylinders. The latter were protected from corrosion by making them subsidiary cathodes. It was hoped to obtain nitric acid from the nitrous fumes, but the process has not proved to be a commercial success. An ingenious process for preparing sodium is due to *Ashcroft*. In this the electrolyte is sodium chloride, which is kept fused by heat generated internally; the separated sodium is collected in lead, which is transferred to a second compartment, and there made the anode of a cell containing fused caustic soda. In this the sodium is dissolved from the lead and precipitated on an iron cathode. The caustic soda undergoes no permanent change, serving merely as a means to transfer the metal from its solution in lead to the final cathode. The Virginia Electrolytic Company are also reported to be using a process based on the electrolysis of fused sodium chloride, chlorine and sodium being obtained directly.

Sodium is a white metal with a pink tinge, of specific gravity 0·97; melting point 95° C. = 203° F.; and boiling point 742° C. = 1,368° F. It oxidises on exposure to air, and decomposes water; it is kept under mineral oil (ordinary kerosene). It is used for reducing other metals—*e.g.*, magnesium—for making sodium amalgam (see *Gold extraction*, p. 339), and for making sodium peroxide. This is effected by placing the sodium on

aluminium trays which are made to traverse a flue through which a current of dried and purified air is travelling in the opposite direction. The metal is thus systematically oxidised to Na_2O_2. The latter is used as a general oxidant, particularly for bleaching, in those cases in which H_2O_2 was formerly employed.

Other important uses of sodium are in the manufacture of artificial indigo, and of a number of other synthetic dyestuffs and of drugs like antipyrin. The major part of the sodium made in England, however, is sent to Glasgow, where it is converted into sodium cyanide by the Cassel Cyanide Company. This is also the chief consumption of the sodium in the United States. Recently sodium has been used for drying transformer oils, and thus improving their insulating qualities.

Potassium may be made by methods similar to those employed for producing sodium. As in the case of sodium, the reduction of the carbonate by carbon is endothermic, an absorption of 194 Cal. taking place. The preparation of the metal is somewhat dangerous, from the formation of a black explosive compound of potassium and carbon monoxide, $K_6(CO)_6$. Potassium is a white metal of a specific gravity 0·87 ; melting point 62° C. = 144° F. ; and boiling point 667° C. = 1,233° F. It forms an alloy with sodium which is liquid at the ordinary temperature, and has been used for the construction of high-range thermometers, indicating temperatures up to 600° C. = 1,112° F.

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